VOLUME 17, NO. 6 JUNE, 1938

REFINER
AND NATURAL GASOLINE MANUFACTURER
A GULF PUBLISHING COMPANY PUBLICATION

The Look Box

Railroads

AN oil burning steam locomotive recently established what is believed to be the longest continuous run by steam locomotive in regular passenger service. Santa Fe engine No. 3461 has made the 2,227-mile run from Los Angeles to Chicago at an average speed of 45 miles per hour. Ordinarily the train on this route requires four locomotive changes for the route includes some of the steepest grades to be found on any railroad in this country.

Through the use of oil-burning engines the railroads are meeting modern demands for increased speed. Fast, clean-burning and efficient fuel oils and automatic lubrication are important factors in the new high-speed engines.

Recognizing the importance of this trend the petroleum refining industry has developed new types of fuel oil to meet the demand of the railroads. More than 55,000,000 barrels of these fuel oils, available in several different grades, are used by the railroads every year. More than 6,000 oil-burning locomotives, including the Diesel-electrics, are powered by petroleum fuels.

The development of automotive type of lubrication for locomotives is an outgrowth of the swing toward longer and faster runs. Locomotives equipped with mechanical lubricators need less terminal servicing. Special lubricants prepared by the refining industry keep the engines running smoothly at climatic temperatures which may vary over a range of 100 degrees on a single trip.

New fuels and special lubricants produced by the petroleum refining industry thus are speeding the railroads towards their goal of fast, economical and comfortable travel.

Taxes

EIGHTEEN cents of every dollar received in 1937 by American oil companies from their customers was required for federal, state, and local taxes, according to estimates made by the American Petroleum Industries Committee. Analysis made by the committee of the 1937 financial statements of 29 representative companies shows that these tax payments amounted to $972,317,838. Included were direct taxes on the operations and properties of the companies, as well as the indirect taxes on gasoline and lubricating oil. More than 60 percent of the oil company receipts went into payrolls and for materials and supplies purchased from scores of other industries.

Representative reports indicate that tax costs of the 29 companies last year exceeded wage payments. For one company, taxes amounted to nearly 17 cents of the gross-receipts dollar, as compared with 13 cents in direct labor costs. Another company reported that taxes were twice as high as payrolls. A third computed taxes at $3,365 per each employee for the year. Dividends of the 29

companies were only one fourth of the taxes, comprising less than 5 cents of the customer's dollar as compared with the 18.5 cents for taxes.

Gasoline taxes collected by the states last year hit a new record high of $756,930,000 last year, a gain of $69,299,000 over 1936, and an increase of $498,091,000 during the past ten years. New York led the states with $61,841,000 in gasoline-tax collections in 1937, a gain of $6,206,000 over 1936. Pennsylvania was second with $55,711,000, followed by California, $46,614,000; Ohio, $46,538,000; Texas, $41,671,000 and Illinois $35,836,000.

Since 1927 the average annual state gasoline tax burden per motor vehicle in the United States has more than doubled. In 1927, when 23,133,000 motor vehicles were registered in this country, $258,839,000 was collected in state gasoline taxes. In 1937 the number of motor vehicles had grown to 29,700,000, an increase of approximately 20 percent over 1927, but state gasoline tax costs had increased by $489,091,000 to a total of $756,930,000, or nearly three times the amount collected a decade ago.

Besides paying state gasoline taxes, which were collected by the oil companies, these companies collected an additional $203,025,000 in federal taxes in 1937. Apparently the oil industry is not only a leading taxpayer among all industries but is likewise one of the best of tax collectors, which work adds greatly to the burden of doing business and aids not at all in efforts toward profitable operations.

A.P.I.

AGAIN this month THE REFINER continues its established policy of publishing the important technical papers presented before the mid-year meeting of the American Petroleum Institute, Division of Refining, held at Wichita, Kansas, late in May. A dozen of these discussions, each correlating and bringing down to date technical and engineering information on a given subject, are included in this issue, all under one cover. The program committee arranging for these excellent papers and the authors presenting them, and the various companies permitting their preparation and presentation are to be complimented, for this program proved to be one of the strongest, technically, that the institute has presented for some time.

Because of the growing use of polymerization processes and other systems using refinery gases which must be clean of hydrogen sulfide, the Division of Refining studied the various gas purification processes available. Thus, in this issue is presented latest information regarding the design, operation and performance of such processes as the sodium phenolate system, the Girbotol process, the Shell phosphate process, and the I. G. Alkacid and I. G. Claus processes. Much of this data has never before been published.

Likewise because of the growing interest in desalting and the variety of fine results to be secured through the removal of salts before petroleum is refined, the division studied the desalting methods and two papers are presented in this issue dealing with the removal of organic salts and with laboratory control of corrosion of distillation equipment and of the desalting processes.

In a special session given over to the study of engineering problems the institute division of refining studied metallurgical topics which are ever of increasing importance to the refiner. From this meeting there are presented papers dealing with the application of Bailey's theory to tube-stress calculations, nickel-bearing alloys used in petroleum refining, and a discussion of new developments in petroleum storage vessels.

Other topics discussed at the mid-year meeting and presented elsewhere in this issue include a report of an investigation in which a model separator was used for determination of data useful in refinery waste water separator design. Another topic of interest and value is the discussion of the identification and the properties of straight-run and cracked residua. In addition one of the major companies has permitted dissemination of data relative to a process for the catalytic hydrogenation of octenes to octanes which likewise appears in this issue. Next month THE REFINER will present certain papers from the meetings of another division of the institute which pertain to certain manufacturing problems in the refining branch of the industry.

The Use of Sodium Phenolate *for* Hydrogen-Sulfide Removal

G. M. CARVLIN
Koppers Company, Pittsburgh, Pennsylvania

THE Koppers phenolate process uses a solution of sodium phenolate to adsorb hydrogen sulfide from refinery and natural gases. The solution is continuously regenerated by means of steam vapor, and the hydrogen sulfide is recovered in practically pure form suitable for conversion to sulfuric acid in a conventional-type acid plant. Acid (of 66-deg.-Baume concentration) may be produced from a typical refinery gas at a total operating cost of $3.25 per ton, with no credit allowed for purified gas or for reduction of maintenance or for elimination of atmospheric pollution. The investment for purification plant and acid plant may be amortized in two years in the typical case cited.

Phenolate-type plants have been in commercial operation approximately two years, total installed capacity being 55,000,000 cubic feet of gas per day. Sulfur-production capacity of these plants is 26,000 tons per year, equivalent to 75,000 tons of 66-deg.-Baume acid. The process is adaptable to a wide range of operating conditions due to flexibility in selection of concentrations of the two chemical constituents, and in design of equipment.

Presented at Eighth Mid-Year Meeting, American Petroleum Institute, Wichita, Kansas, May 24, 1938.

DURING the last several years there has been a rapidly-growing realization that the recovery of sulfur from cracking-still gases is an objective meriting the serious consideration of all refinery operators. It is the purpose of this paper to present a general review of this subject, with particular reference to the Koppers phenolate process in its theoretical aspects and commercial applications.

Prior to 1936, the primary reason for purifying refinery gas was to prepare it for distribution for domestic and industrial uses where the presence of sulfur would be most undesirable and where legal restrictions make the removal of hydrogen sulfide mandatory. The trend toward purification of refinery gas has recently been accelerated by the increasing importance of three other major influences, viz:

1. Extensive application of processes for the polymerization of hydrocarbons contained in refinery gas, and the advisability of charging gases low in sulfur to these units in order to obviate serious corrosion of equipment and to minimize the expense of de-sulfurizing the final liquid product.

2. The development of purification equipment capable of recovering substantially pure hydrogen sulfide which is readily convertible to sulfuric acid by any of the conventional acid manufacturing processes.

3. Maintenance expense for steel parts of furnaces and other refinery equipment due to corrosive attack of the products of combustion of high-sulfur gases when used for fuel. Furthermore, the sulfur dioxide and sulfur trioxide released to the atmosphere in these flue gases constitute a serious pollution nuisance in many cases.

Thus it may be demonstrated that sulfur recovery constitutes one of those gratifying developments which afford an opportunity to recover, as a profitable by-product, a material which has previously been one of the most serious nuisances connected with refinery operation.

HISTORICAL

The first liquid de-sulfurization process, called the "Seaboard process," and employing a solution of sodium carbonate, was developed by Koppers Company in 1920 for the purification of coal gas. This may rightfully be said to mark the beginning of a new era in the removal of hydrogen sulfide from gas, inasmuch as it substituted for the cumbersome and labor-consuming iron-oxide boxes a compact and substantially automatic method of removing the hydrogen sulfide by a circulating solution.

Not only was the Seaboard process the pioneer liquid-purification process, but it possesses some virtues of simplicity and economy that make it adaptable to certain conditions today despite the later development of other improved processes that are more generally useful for most conditions. Some 60 Seaboard plants have been built to purify various kinds of manufactured gases. Fifteen have been built to purify natural gas, and installations have been made in seven of the largest refineries of the country. These plans have, without exception, proved to be economical and efficient for the treatment of gases containing hydrogen-sulfide concentrations varying from 50 grains to 6000 grains per 100 cubic feet (0.1 to 10 percent), and in the presence of carbon-dioxide concentrations as high as 15 percent and oxygen concentrations of several percent.

The Seaboard process has been applied successfully in commercial practice to the removal of hydrogen sulfide from liquid hydrocarbons of various physical characteristics, the only modification required in the usual gas-purification scheme being substitution of a liquid-liquid contactor for the usual packed

or bubble-tray absorber and the addition of a continuous separator.

The two principal faults inherent in the Seaboard process are:

1. Hydrogen sulfide removed from the gas is discharged from the purification plant as hydrogen-sulfide gas mixed with several hundred times its volume of air. Under some conditions this hydrogen-sulfide-containing air may be released directly to the atmosphere, or it may be used as combustion air in boilers, furnaces, etc. Under no practical conditions may sulfur be recovered, so that the Seaboard process is essentially only a gas-purification process with no by-product credit to offset expenses.

2. In the purification of the high-sulfur natural and refinery gases usually encountered, it is necessary to circulate large volumes of solution due to the comparatively low carrying capacity of the weak sodium-carbonate solution employed. Inasmuch as these gases are usually treated at fairly high pressures, the power required for circulating solution results at times in inordinately high operating cost.

In an effort to correct these deficiencies, Koppers Company developed several so-called "hot-actification" systems using various solutions for absorbing the hydrogen sulfide, but all having one common feature, viz., that the foul solution from the absorption step is regenerated by boiling, whereby the sulfur is expelled as practically pure hydrogen-sulfide gas saturated with water vapor. The absorbents we have used are all fairly concentrated solutions of alkaline reagents having a high carrying capacity for hydrogen sulfide, such as sodium carbonate, potassium borate, magnesium hydroxide, and sodium phenolate. The later reagent is the most recently developed, and has had the most extensive practical application.

The general class of purification processes designed to recover hydrogen sulfide in the form of elemental sulfur should receive brief mention here. These processes which have been applied commercially by Koppers Company to the purifiaction of manufactured gases have met with considerable success, both in this country and abroad. The three most important processes in this group use alkaline solutions containing iron, nickel, and arsenic salts; and all utilize a similar principle of operation. The foul solution is regenerated by contacting with air, whereupon sulfur is liberated in finely-divided form and separated from the solution as a froth—which is further de-watered and sold in the form of paste containing about 50 percent water. This sulfur paste has found wide acceptance as a fungicidal spray, and commands a considerably higher price than natural sulfur in its various commercial forms.

Elemental-sulfur recovery processes have not as yet been applied to the treatment of refinery gas—although such application is being seriously considered by some refiners, particularly for the treatment of gas under low pressure or for the conversion of hydrogen sulfide, produced by the hot-actification processes, to elemental sulfur.

THEORY OF THE PHENOLATE PROCESS

The ideal liquid for absorbing an acidic gas such as hydrogen sulfide is obviously a strongly-alkaline solution; and, consequently, sodium-hydroxide solutions have long been used for the purpose. It is well recognized, however, that regeneration of the resultant sodium-hydrosulfide solution is not economically feasible due to the huge quantities of steam or other energy input required. This energy requirement may be brought within reasonable limits by adding to the caustic solution an auxiliary acidic constituent which has an acidity less than that of hydrogen sulfide at normal temperatures. A great many acids meet the condition, but there is another very important condition to be met that distinctly limits the number of acidic compounds available. Unfortunately, hydrogen sulfide has the property of increasing in acidity with temperature, so that it tends to be held more firmly by the sodium hydroxide at the boiling temperature—and it is a necessary function of the auxiliary acidic constituent to overcome this tendency. This can be accomplished by using an acid which will increase in acidity with temperature rise at about the same rate as the hydrogen sulfide. Under these conditions, the auxiliary acidic constituent will tend to "crowd out" the hydrogen sulfide on actification at the boiling temperature.

The above desirable conditions are admirably met by certain phenols as shown by the fact that the electrolytic dissociation constant of phenol is 1.3×10^{-10}, while that of hydrogen sulfide is 5.7×10^{-8}. This shows that the phenol is a considerably weaker acid than hydrogen sulfide at normal absorption temperatures, and thereby satisfies the first condition named above. Furthermore, the increase in acidity of phenol with temperature rise is almost exactly the same as that of hydrogen sulfide, as shown by the fact that the molecular heat of electrolytic dissociation of phenol is —6100 calories, while that of hydrogen sulfide is —6060 calories. Thus it may be seen that the use of sodium-phenolate solution for gas purification is theoretically sound, and that the following reaction is readily reversible within the limits required in practical application:

$$NaOC_6H_5 + H_2S \rightleftharpoons NaHS + C_6H_5OH$$

APPLICATION OF THEORY TO DESIGN OF PLANTS

The use of a solution, containing in combination an absorption agent and an auxiliary acidic constituent as described above, permits a wide flexibility in the choice of solution for any given set of operating conditions. For example, if the gas contains only a small amount of hydrogen sulfide, and a very high degree of removal is desired, the solution selected will be one containing a fairly low concentration of caustic and proportionately high concentration of phenol in order that the solution entering the absorber will be actified to the low hydrogen-sulfide equilibrium required. On the other hand, if the gas contains a high concentration of hydrogen sulfide and the primary object is to recover sulfur, the solution selected will contain a comparatively high concentration of caustic with a low ratio of phenol to caustic. In general, the phenolate process requires solution circulation rates amounting to only about one-thirtieth of the rates required by the Seaboard process.

The Koppers two-stage phenolate process has been developed to effect the maximum steam economy in instances where large quantities of sulfur are to be removed, and where the steam or other heat consumption is a vital item in the operating expense. The two-stage process is recommended also in cases where virtually complete removal of hydrogen sulfide is required.

Figure 3 contains a chart showing the relations

TABLE 1

	Single-Stage System	TWO-STAGE SYSTEM		
		Primary Stage	Secondary Stage	Total of Both Stages
Grains hydrogen sulfide per 100 cu. ft. in inlet gas	6,000	6,000	2,000	6,000
Grains hydrogen sulfide per 100 cu. ft. in outlet gas	80	2,000	80	80
Grains hydrogen sulfide removed	5,920	4,000	1,920	5,920
Grains hydrogen sulfide per gallon of fresh solution	3,800	6,770	3,800	....
Grains hydrogen sulfide per gallon of foul solution	7,460	7,460	6,770	....
Grains hydrogen sulfide per gallon of solution	3,660	690	2,970	....
Grains hydrogen sulfide per 100 cu. ft. of steam entering actifier	0	3,000	0	0
Grains hydrogen sulfide per 100 cu. ft. of steam leaving actifier	4,500	9,000	3,000	9,000
Grains hydrogen sulfide per cubic foot of steam	45	60	30	90
Pounds of steam required per 1,000 cu. ft. of gas	52.6	26.7	25.6	26.7

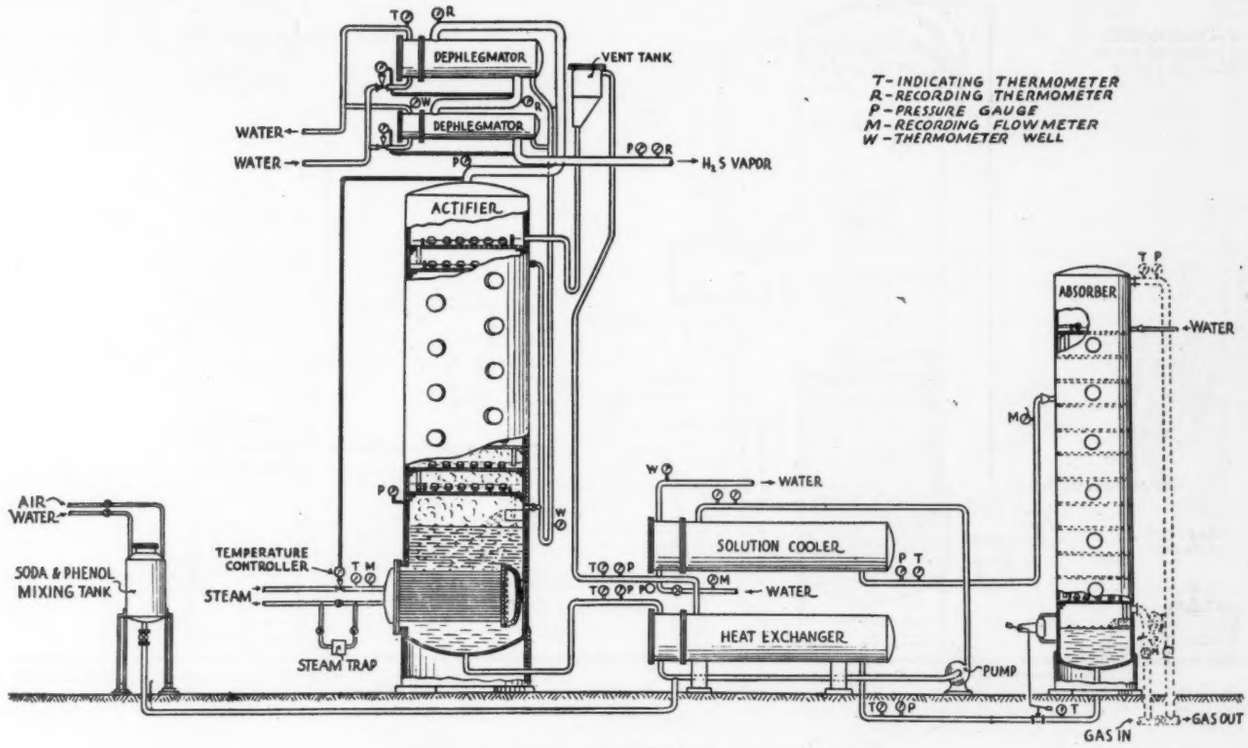


FIGURE 1
Flow Diagram of Single-Stage Phenolate Process.

between partial pressures of hydrogen sulfide and the hydrogen-sulfide content of the solution under the conditions existing in the absorption and actification stages for both the single-stage and two-stage systems. This chart is based on a set of operating conditions which is fairly typical of refinery-gas purification. The gas to be purified contains 6000 grains of hydrogen sulfide per 100 cubic feet, and the exit gas contains 80 grains per 100 cubic feet measured at the actual pressure existing in the absorber. The solution used in this case contains 4 moles of sodium hydroxide and 2.5 moles of phenol per liter. Curve **AB** in Figure 3 represents the vapor pressure of dissolved hydrogen sulfide over this solution at 25° C. Curve **CD** represents the vapor pressure of the solution at its boiling point.

In the specific example which we have taken, the hydrogen-sulfide content of the actified solution in equilibrium with the exit gas is 3800 grains per gallon, and that of the foul solution in equilibrium with the entering gas is 7460 grains per gallon. The vapor pressure of hydrogen sulfide in phenolate solutions does not follow Henry's law; and, as a result, the vapor-pressure curves are strongly bowed. Actual operating conditions are illustrated by straight lines on the chart. Thus the dotted line **FH** shows the operation of the single-stage absorber, point **F** corresponding to the hydrogen-sulfide content of gas leaving the absorber, and of actified solution in equilibrium with it. Point **H** corresponds to the hydrogen-sulfide content of gas entering the absorber, and of solution in equilibrium with it.

Operation of the primary absorber of the two-stage system is illustrated by the line **GH**, the point **G** corresponding to the hydrogen-sulfide content of the solution entering the primary absorber and the hydrogen-sulfide content of the gas leaving the primary absorber. The line **FG** illustrates the operation of the secondary absorber of the two-stage system.

Slopes of the operating lines (**FH, FG,** and **GH**) determine the ratio of solution to gas required in the absorber for the single and two-stage systems. The slope of the line **FG**, which is comparatively flat, corresponds to the low rate of re-circulation in the secondary system; while the slope of the line **GH**, which is quite steep, corresponds to a much higher

rate of re-circulation in the primary system. The solution circulation rate indicated by the line **FH** for the single-stage absorber lies between the rates for the primary and secondary absorbers in the two-stage system.

The principal advantage of the two-stage system may be seen from a study of the operating lines for the actifiers. The line **KL** represents the operation of the single-stage actifier, showing actification of the solution from a concentration of 7460 grains of hydrogen sulfide per gallon to 3800 grains per gallon. The slope of this operating line is comparatively flat, and the distance between **KL** and the curve **CD** increases rapidly as the concentration of hydrogen sulfide in the solution increases. This characteristic limits the steam economy of the single-stage system, and it may readily be seen that the addition of a second actification stage causes the operating curve of the actifier to approach more closely the vapor-pressure curve of the boiling solution. If several stages of actification were used, a corresponding number of operating lines joining at various angles would result—and a still closer approach to the curve representing the vapor pressure of the solution would be effected.

Inasmuch as the slope of the line **MN** is much steeper than that of the line **KM**, it follows that the steam required for actification per gallon of solution in the primary actification stage is very much less than the steam required per gallon in the lower or secondary-stage actifier section. Consequently, the rate of solution circulation of the primary system is relatively high, and the steam required for actification per gallon of solution is relatively low as compared to the secondary system. Inasmuch as the steam employed in the secondary actifier is later used in the primary actifier, and inasmuch as the two systems are in balance as regards steam requirement, the net result is to lower the total steam consumption for the plant very materially. Table 1 shows a comparison of actual steam requirements per 1000 cubic feet of gas purified for the single and two-stage systems according to the given set of conditions.

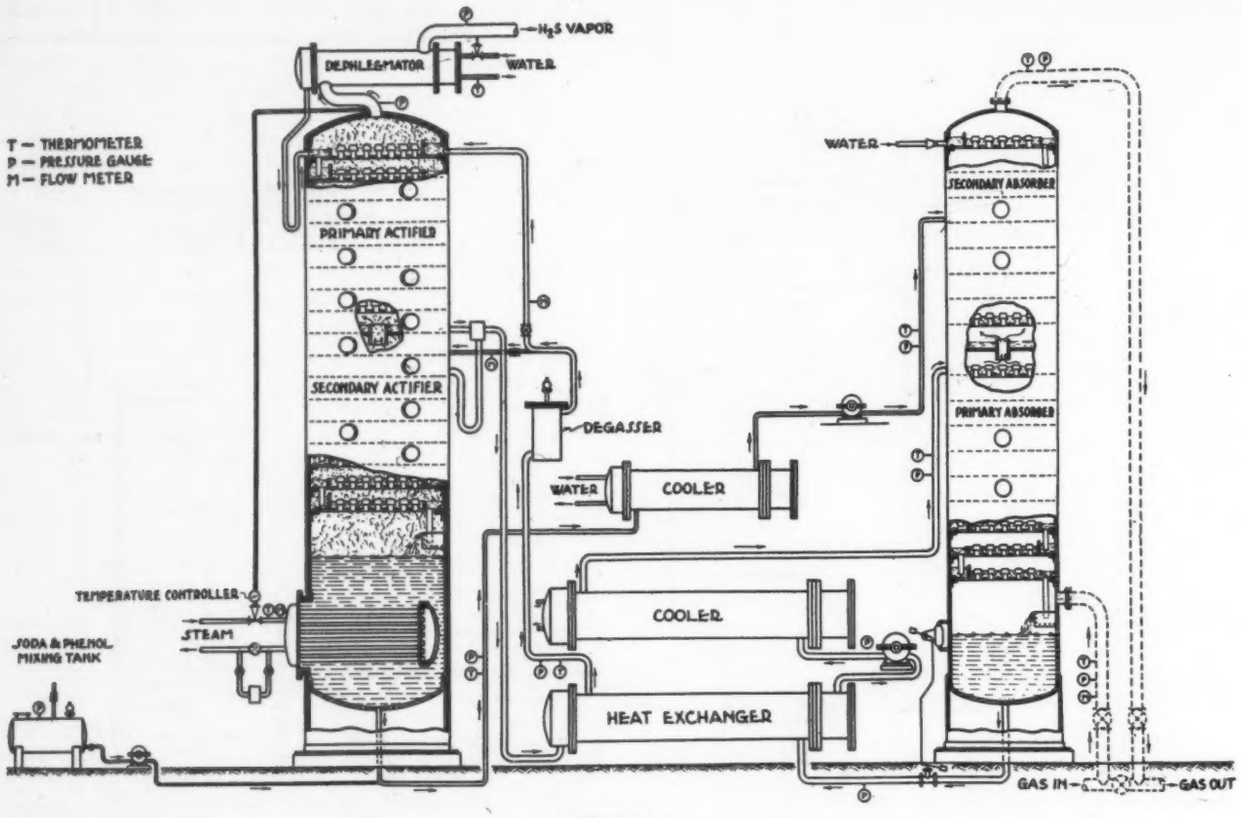


FIGURE 2
Flow Diagram of Two-Stage Phenolate Process.

METHOD OF OPERATION

Operation of the single and two-stage phenolate systems is illustrated by flow diagrams in Figures 1 and 2, respectively. The single-stage system comprises a continuous cyclic operation, similar to the familiar system used for absorption and recovery of gasoline from natural gas. Gas enters the bubble-tray absorber at the base, and leaves at the top after passing through a series of bubble-cap trays countercurrent to the flow of actified phenolate solution which enters the column on the fourth tray from the top. A very small volume of fresh water is introduced continuously on the top tray to scrub out and return to the solution any chemicals entrained in the gas. The foul solution is forced by the gas pressure from the reservoir in the base of the absorber through the heat exchanger to the top of the actifier column. The solution flows down the actifier countercurrent to a stream of steam which is released from the solution itself by the reboiler in the base of the column. The actified solution flows by gravity through the heat exchanger to the suction of the circulating pump, which forces it through a tubular cooler, and thence to the inlet of the absorber—where the cycle again begins.

Hydrogen sulfide released in the actifier passes through the dephlegmator, where the accompanying water vapor is condensed and returned to the actifier column. The hydrogen sulfide, having a purity of 95 to 99 percent (exclusive of water vapor) then passes on to the acid-plant burner or other point of disposal. The dephlegmator in this diagram contains two sections, and this is recommended as a measure for conserving water only in cases where large quantities of hydrogen sulfide are produced.

The functioning of the plant is almost entirely automatic. Steam to the reboiler is controlled automatically by the temperature of the vapors leaving the actifier. Water to the dephlegmator is controlled by the temperature of the vapor leaving the dephlegmator. It is necessary to add phenol only at intervals of several weeks.

The operation of the two-stage system differs from the single-stage operation, as outlined above, in the following particulars:

The major portion of the solution is withdrawn from the actifier about midway of the column, and is introduced into the absorber about half way down the column after passing through the heat exchanger and cooler. The minor part of the solution continues down to the base of the actifier, and in the course of this travel is contacted with a proportionately large amount of fairly clean steam. This small volume of highly actified solution is pumped through a cooler to the upper section of the absorber. After flowing through the secondary absorber, this solution joins the main body of solution in the primary absorber, and the entire volume of solution is forced by the gas pressure through the heat exchanger to the top of the actifier column.

PHENOLATE PLANTS OPERATING ON REFINERY GAS

Figure 4 shows a photographic view of the columns in a phenolate plant built by Koppers Company for a large refinery on the Pacific Coast. This plant has a capacity of 16,500,000 cubic feet of gas per day containing 4 to 5 percent of hydrogen sulfide (2500 to 3200 grains per 100 cubic feet). The recovery of sulfur at capacity operation amounts to 35 tons per day. The recovered hydrogen sulfide is forced by actifier pressure through a pipe line over a mile long to a contact-type sulfuric-acid plant, where it is converted to sulfuric acid. The dark insulated column in the photograph is the actifier. The other two columns are absorbers handling separate streams of gas at pressures of 5 pounds and 150 pounds. The gas temperature is approximately 100°F. The lower section of the taller absorber comprises the degasser, where absorbed hydrocarbon gases are released from the foul solution before it proceeds to the actifier.

TABLE 2

Daily Material Balance

Gas Treated, cu. ft	20,000,000
Pressure, lb., per sq. in	100
Temperature, deg. C	25
Hydrogen-sulfide concentration, grains per 100 cu. ft	1,000
Hydrogen sulfide recovered (95 percent removal), tons	13.6
Sulfur equivalent, tons	12.8
100 percent sulfuric acid produced (95 percent conversion), tons	37.2
Sulfuric acid (66 deg. Baume) produced, tons	34.6
Value of acid (66 deg. Baume) at $13.50 per ton	$467.10

Aggregate Daily Operating Cost for Purification and Acid Plant

Labor: one man, 24 hours at $0.80	$19.20
Laboratory and supervision	5.00
Steam: 180,000 lb. at $0.20	36.00
Power: 2,400 kwh. at $0.005	12.00
Water: 790,000 gallons at $0.015	11.90
Phenol: 90 lb. crude tar acid at $0.10	9.00
Supplies	3.50
Maintenance	15.00
	$111.60
Operating cost per ton of acid (66 deg. Baume)	$3.25
Net return before fixed charges	$355.50
Annual return before fixed charges (350-day year)	$126,000
Annual return on investment (approximate), percent	50

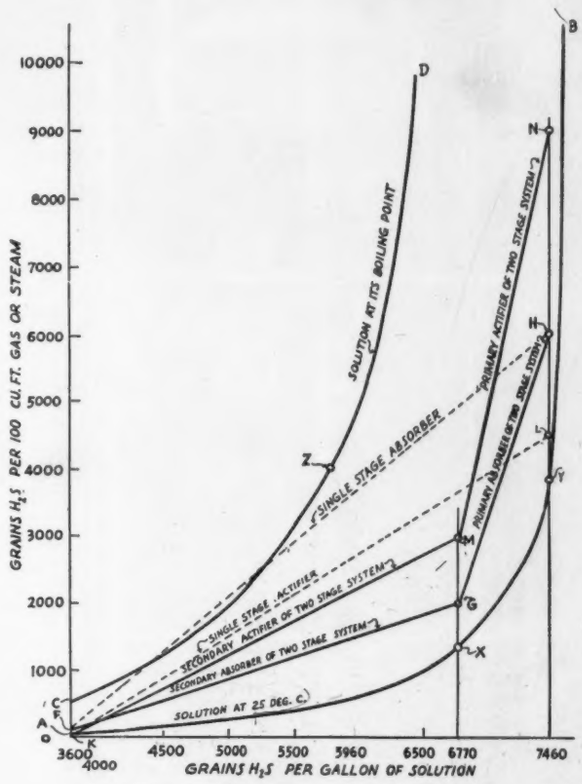


FIGURE 3

Chart Showing Relations Between Partial Pressures of Hydrogen Sulfide and Hydrogen-Sulfide Content of Phenolate Solution.

Figure 5 is another view of this plant showing a novel feature in its design, viz., the gas-tight steel enclosure around the towers and tubular equipment. This housing was specified by the purchaser as a safety feature to eliminate possible hazards from the toxic hydrogen sulfide, in the event of rupture of the vessels or piping. All control valves are located adjacent to a platform along the outside of the enclosure. The back of the instrument panel may be seen forming one side of the control house at the right of the photograph.

The primary purpose of this installation is to recover sulfur for the manufacture of sulfuric acid. Another advantage gained by purifying these fuel gases is the elimination of corrosion around the furnaces and correction of atmospheric pollution by the sulfurous flue gases. This plant has been in operation for almost two years, and has consistently recovered 96 to 98 percent of the hydrogen sulfide from the gas at a low cost per ton of sulfur equivalent.

Figure 6 shows a photograph of a phenolate plant installed by Koppers Company in a large Eastern refinery. This plant has a capacity to purify 23,000,000 cubic feet per day of refinery gas containing

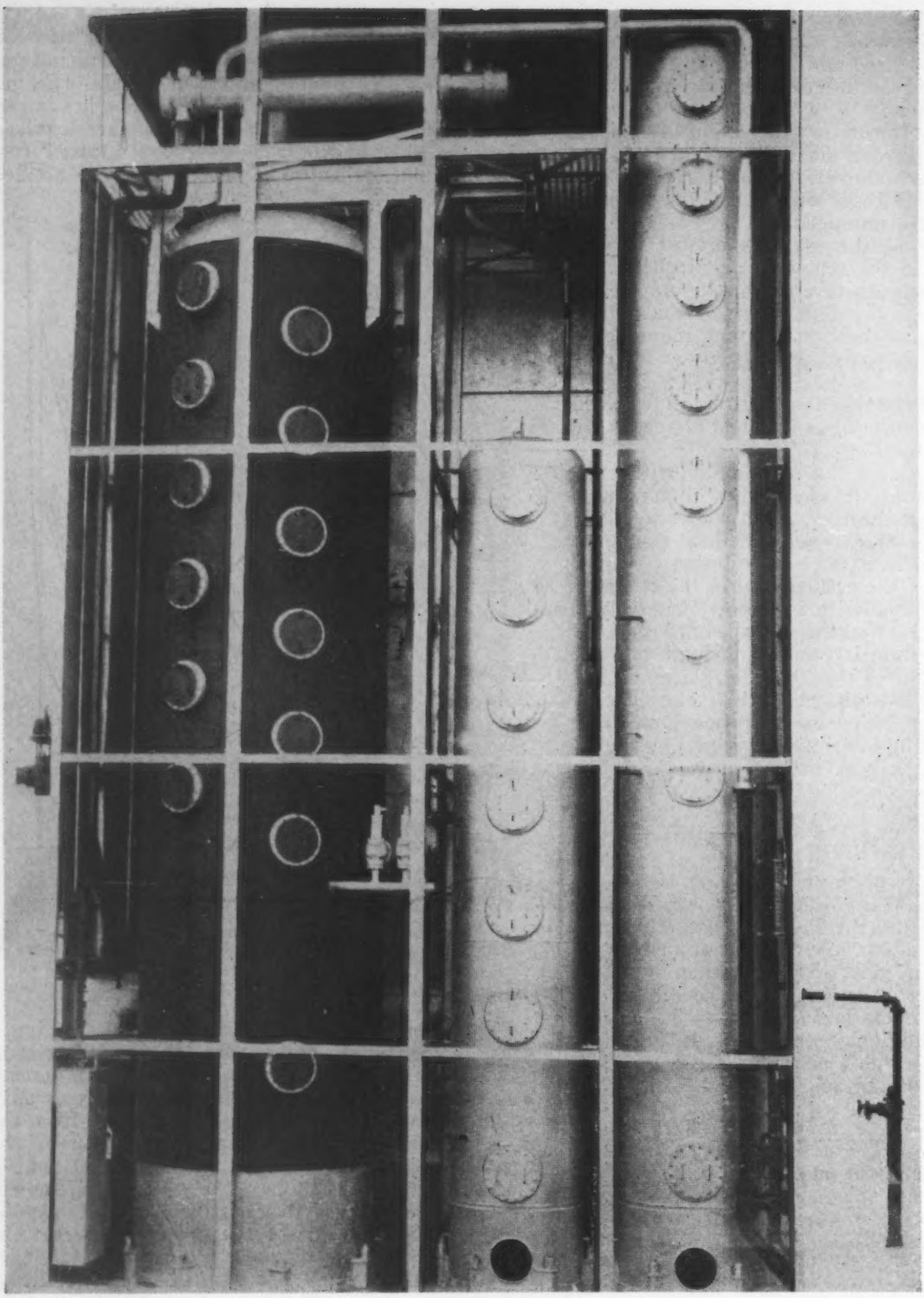


FIGURE 4
View of Columns in a Phenolate-Process Plant.

about 1½ percent hydrogen sulfide (1000 grains per 100 cubic feet). The gas is treated at a pressure of 225 pounds in two separate streams, and at a temperature of approximately 125°F. Hydrogen sulfide recovered in this plant is also piped a distance of approximately one mile to a contact-type acid plant, where it is converted to sulfuric acid for use in the refinery. In contrast to the plant described above, all equipment here is out of doors.

The primary purpose of this installation is to remove 95 percent of the hydrogen sulfide from gas which is to be fed to a polymerization plant, and the recovery and utilization of the sulfur are of secondary importance.

Phenolate-type plants now in operation have an aggregate capacity to purify 55,000,000 cubic feet of gas per day. Total sulfur-recovery capacity of these plants is 26,000 tons per year, corresponding to approximately 75,000 tons of 66° Baumé acid.

SULPHURIC-ACID PRODUCTION COST

Table 2 shows the cost of producing sulfuric acid from hydrogen sulfide in a fairly typical refinery gas. The gas contains 1000 grains of hydrogen sulfide per 100 cubic feet, and is purified at approximately 100° F. No particular pressure is specified, inasmuch as the operating costs are not seriously affected by the pressure in the absorption stage. Obviously, the pressure of the gas does have a material influence on the size of the equipment and, consequently, on the cost of the plant.

It is apparent that the largest single item of operating cost is that for steam to actify the solution. A large part of the required steam may be recovered in the acid plant from heat of combustion of the hydrogen sulfide when the volume of hydrogen sulfide burned is sufficient to justify the expenditure for a waste heat boiler. (Hydrogen sulfide has a caloric value of 655 B.t.u. per cubic foot.) In cases where fuel gas is relatively cheap as compared to steam, a gas-fired reboiler may be used in the actification stage. This has been done on one natural-gas purification plant where no steam-generating equipment was available.

SULFURIC-ACID PLANT OPERATION

Hydrogen-sulfide gas from the phenolate-plant actifier will be saturated with water vapor at cooling-water temperature, and will contain from 1 to 4 per-

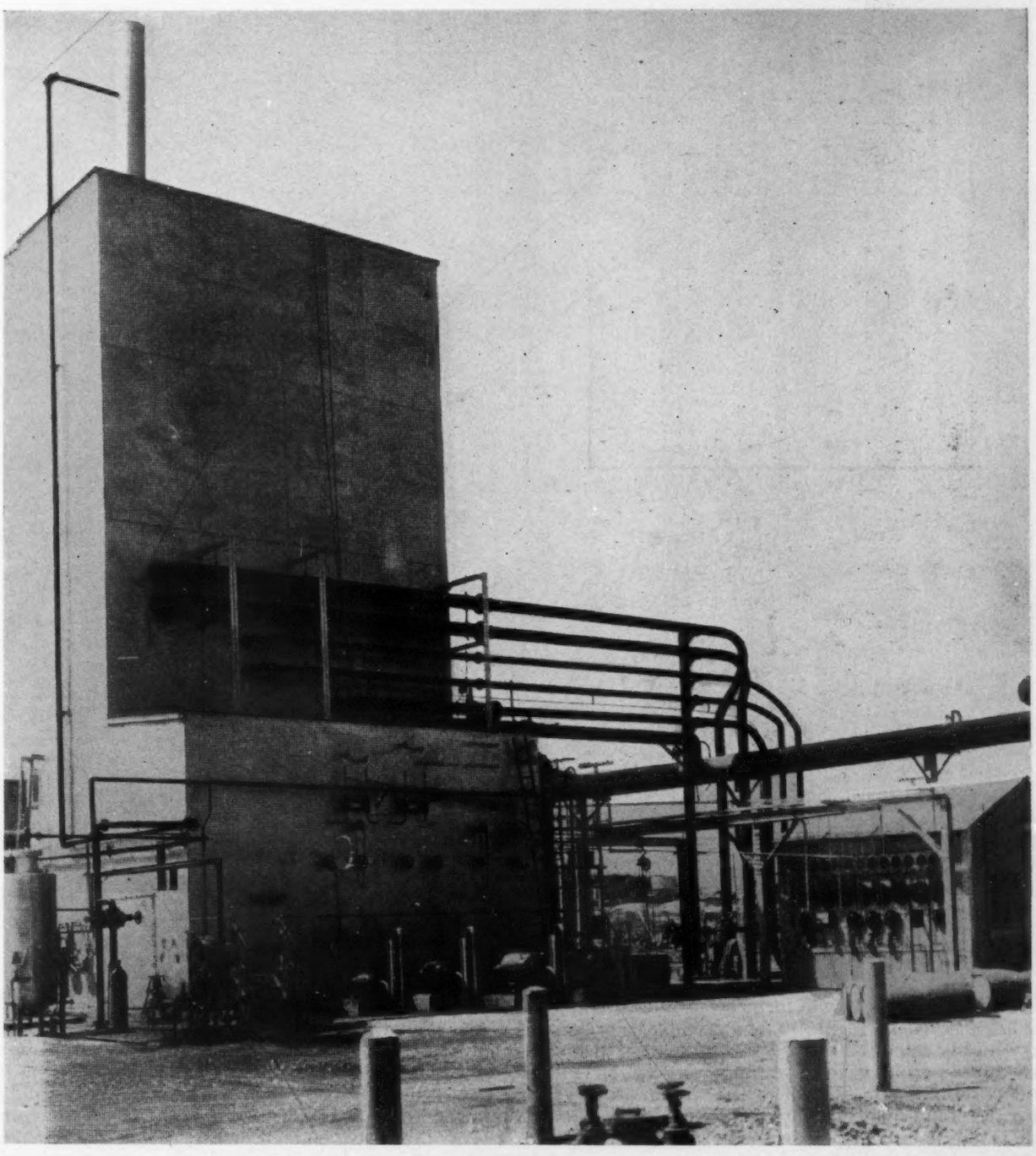


FIGURE 5
Phenolate-Process Plant with Columns Enclosed in Steel Shell.

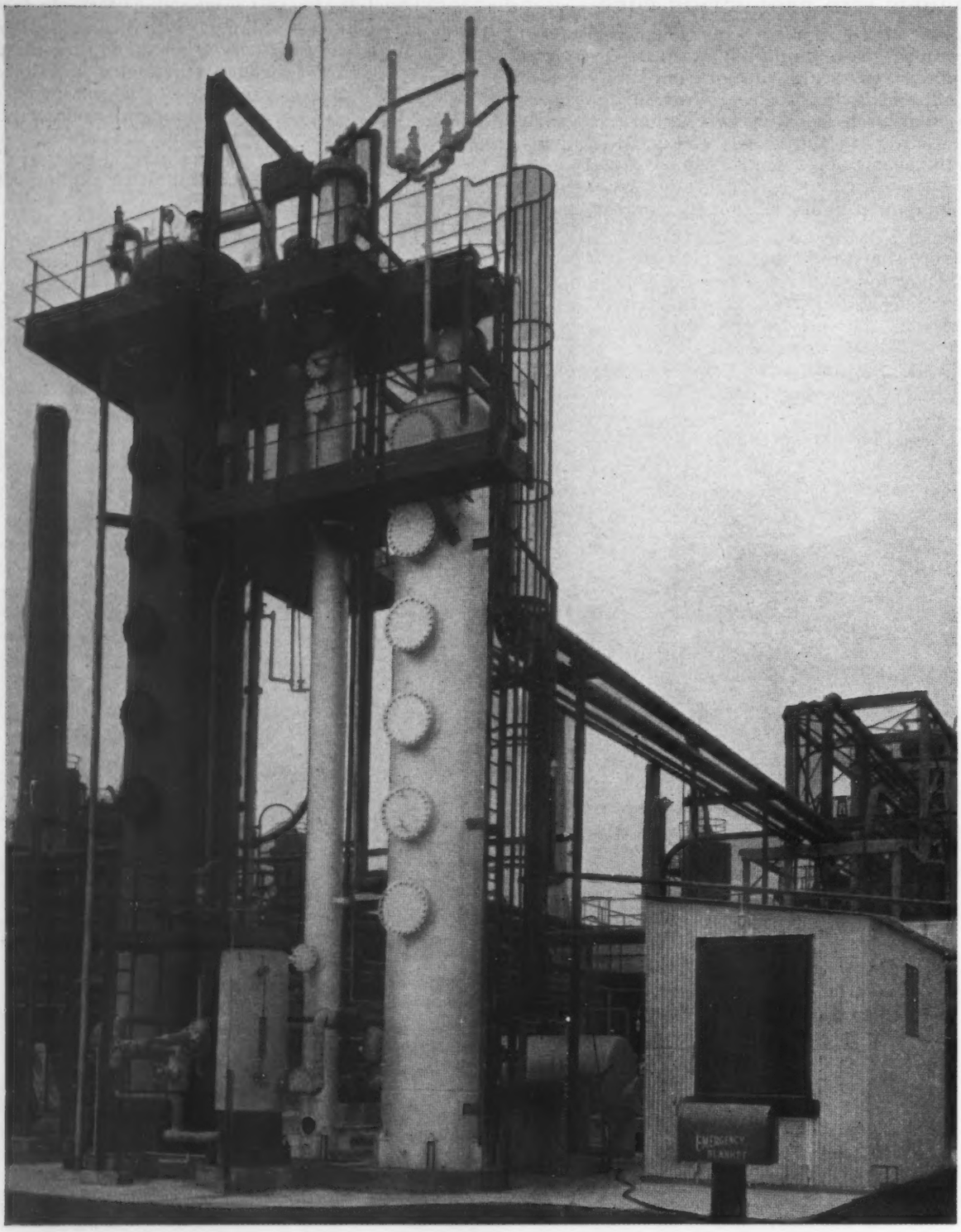


FIGURE 6
Phenolate-Process Plant Showing Absorbers, Actifier, and De-gassor.

cent of impurities in the form of carbon dioxide and hydrocarbons. Incidentally, the phenolate process is very highly selective toward the absorption of hydrogen sulfide from gases containing hydrogen sulfide and carbon dioxide, so that the amount of carbon dioxide contaminating the recovered hydrogen sulfide is slight in comparison to contamination encountered in other sulfur-recovery processes.

Water vapor present in the hydrogen sulfide and water formed in its combustion necessitate the use of a so-called "purification-type" acid plant, inasmuch as the sulfur dioxide entering the converter must be bone dry for American acid plants. Figure 7 illustrates the flow of materials through the "purification-type" contact acid plant. Hydrogen sulfide is burned in a refractory-lined burner, and the combustion products (mixed with secondary air in an amount necessary to provide the proper ratio of sulfur to oxygen) pass through a waste heat boiler to a cooling tower—where the gases are cooled by water

or weak acid in a closed circulation system. The cooled gases pass through a Cottrell precipitator or coke filter, to eliminate entrained mist, into a drying tower—where they are scrubbed with 98-percent sulfuric acid. The bone-dry gases are then forced by a blower through a heat exchanger and into the converter. Here the hot gas passes through the vanadium or platinum mass, and the sulfur dioxide is converted to sulfur trioxide. After the converter, the gases exchange heat with the cold incoming gases, and enter the final absorbing tower—where the sulfur trioxide is absorbed in 98-percent acid. The final product is removed from this circulation system, and it may be converted to weaker acid or to oleum by brief additional processing. The inert gases, consisting of nitrogen, carbon dioxide, oxygen, and traces of sulfur dioxide, are released to the air through a stack on top of the absorber. Normal conversion efficiency from hydrogen sulfide to sulfuric acid is about 95 percent of stoichiometric equivalent.

Hydrogen sulfide may be converted to sulfuric acid in existing chamber-type plants, but no description of application to the chamber process will be attempted here, inasmuch as it is unlikely that any new chamber installations will be made for this purpose.

The burning of hydrogen sulfide bears the same relation to the burning of brimstone or pyrite, as regards convenience of operation and control, as the burning of gaseous fuel in any furnace bears to the burning of solid fuel.

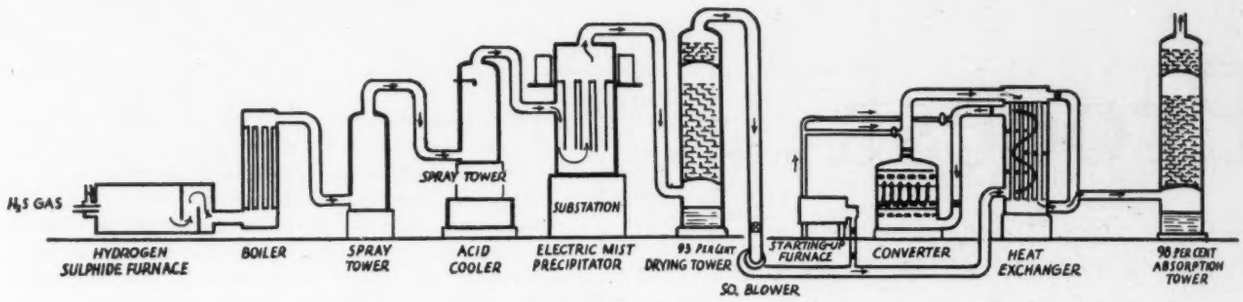


FIGURE 7
Flow Diagram of "Purification-Type" Contact Acid Plant.

SUMMARY

The Koppers phenolate process uses a solution of sodium phenolate to absorb hydrogen sulfide from refinery and natural gases. The solution is continuously regenerated by means of steam vapor, and the hydrogen sulfide is recovered in practically pure form suitable for conversion to sulfuric acid in a conventional-type acid plant. Acid (of 66° Baumé concentration) may be produced from a typical refinery gas at a total operating cost of $3.25 per ton, with no credit allowed for purified gas or for reduction of maintenance or for elimination of atmospheric pollution. The investment for purification plant and acid plant may be amortized in two years in the typical case cited.

Phenolate-type plants have been in commercial operation approximately two years, total installed capacity being 55,000,000 cubic feet of gas per day. Sulfur-production capacity of these plants is 26,000 tons per year, equivalent to 75,000 tons of 66° Baumé acid. The process is adaptable to a wide range of operating conditions due to flexibility in selection of concentrations of the two chemical constituents, and in design of equipment.

The Girbotol Purification Process . . .

W. R. WOOD and B. D. STORRS
The Girdler Corporation
Louisville, Kentucky

THE Girbotol process is a simple, cyclic process for separating hydrogen sulfide and carbon dioxide from gaseous mixtures. It is efficient and economical in operation. Hydrogen sulfide and carbon dioxide are recovered in concentrated form. The process is unique in that a one-component absorbent is used. The absorbents, the aliphatic amines, are stable and relatively non-volatile.

The Girbotol process is described, and its wide application illustrated.

Use of the process for the simultaneous purification and dehydration of gases is also discussed.

Presented at eighth mid-year meeting, American Petroleum Institute, Wichita, Kansas, May 24, 1938.

REMOVAL of hydrogen sulfide from hydrocarbon gases is a process of growing importance at the present time. In the refinery field, polymerization, the production of liquefied hydrocarbon gases, the synthesis of isooctane, hydrogen, and various organic chemicals such as the aliphatic alcohols, all are improved by the use of sulfur-free starting materials. In some instances catalysts are injured by hydrogen sulfide. In others, expensive after-treatment or methods which impair the quality of the finished product must be resorted to if hydrogen sulfide is present in the charge. In all cases the corrosive effects of hydrogen sulfide on the process equipment are eliminated by its removal. As new methods for converting the lighter components of refinery gases into marketable products are developed, removal of hydrogen sulfide will become increasingly necessary because hydrogen sulfide, due to its vapor pressure, tends to accumulate with these more volatile fractions. The Girbotol process† is an efficient method for removing hydrogen sulfide and other weak acidic gases from gas mixtures.

THEORY AND DESCRIPTION OF PROCESS

The Girbotol process originated with the discovery that acidic gases such as hydrogen sulfide and carbon dioxide react with certain amines to form compounds which may be broken down by heat. This reversible reaction may, in the case of hydrogen sulfide, be represented as follows:

$$RNH_2 + H_2S \rightleftharpoons RNH_3HS$$

Where: R represents an organic residue.

The equilibrium proceeds to the right or left depending on the temperature, and on the partial pressure of hydrogen sulfide. In a Girbotol plant, hydrogen sulfide is washed from a gas mixture at one temperature at the beginning of the cycle and expelled from the amine solution at a higher temperature in a subsequent part of the cycle. Water solutions of the amines are usually employed. The cycle is continuous, and the hydrogen sulfide is recovered in concentrated form.

Figure 1 shows a typical flow diagram of the Girbotol process. Sour gas containing hydrogen sulfide flows into the base of the absorber, which is a bubble plate or packed tower. Lean amine solution enters the absorber near its top and flows in countercurrent relation to the rising gas, absorbing hydrogen sulfide in its downward passage, Gas free from hydrogen sulfide leaves from the top of the absorber.

Rich amine solution containing the removed hydrogen sulfide flows by absorber pressure, or is pumped, from the base of the absorber through the heat exchanger, and thence into the upper section of the reactivator. If the treating pressure is high, and if an extremely pure hydrogen sulfide is desired, a flash drum, operating at a lower pressure than the absorber, is placed between the absorber and the heat exchanger for releasing hydrocarbons dissolved in the solution due to the high treating pressure.

The reactivator is a bubble plate or packed tower. In or near its base there is the reboiler, which is an indirect heating element supplied with low-pressure steam or other suitable medium for boiling the amine solution and expelling the hydrogen sulfide. As the solution flows down through the reactivator, it is heated by ascending steam generated by the reboiler, and the hydrogen sulfide is expelled. In the reboiler the solution reaches its boiling point, slightly above the boiling point of water at the pressure of the reactivator.

Regenerated amine solution free from hydrogen sulfide is pumped from the base of the reactivator through the heat exchanger, then through the solution cooler, and back to the top of the absorber.

Hydrogen sulfide and steam flow together from the top of the reactivator to the hydrogen-sulfide cooler, where the temperature of the mixture is re-

† Patents on the Girbotol process are owned by The Girdler Corporation, Louisville, Kentucky.

$190^{\circ}F$
$220^{\circ}F$

duced to atmospheric and the steam condensed. The condensate returns to the top of the reactivator, and concentrated hydrogen sulfide flows from the cooler.

All of the equipment is standard, similar in design to a refinery absorption plant.

The plant is made fully automatic in operation by the use of suitable control equipment. No labor is required during routine operation except for control tests and for normal maintenance. The utilities needed for operation are exhaust steam, or its equivalent, for heating, water for cooling, and power for pumping the solution. Mechanical losses of amine solution are small, and the amine itself lasts indefinitely. Vaporization losses with monoethanolamine, a comparatively volatile amine, are as low as one-tenth of a pound per million feet of gas treated.

The Girbotol absorbents are not corrosive toward steel or iron. Because the solutions are alkaline at all times, the corrosive effects of hydrogen sulfide are practically negligible. Low-carbon steel and cast iron are suitable construction materials for all portions of the plant, and no special alloys are required.

A number of amines suitable for use in the Girbotol process are available commercially at reasonable cost. Since each differs slightly in its physical properties from the others, there is a group of absorbents from which the proper amine may be selected for any particular purification plant. All of the amines which are used have the desirable characteristics of high capacity for hydrogen sulfide and carbon dioxide, rapid rate of reaction with the acidic gases, and low volatility. These amines are miscible with water in all proportions. Because the amines have high capacities for acidic gases, dilute water solutions may be circulated. This results in a small initial expenditure and low replacement costs for the reagent.

The amines are organic bases, derivatives of ammonia; and, like ammonia, react rapidly with acidic gases such as hydrogen sulfide and carbon dioxide to form hydrosulfides and carbonates. Until a high percentage of the available amine has been neutralized, the resulting solution has a negligible acid-gas vapor pressure. By carrying out the absorption in a countercurrent contractor, the acidic component of a gas stream may be stripped out completely.

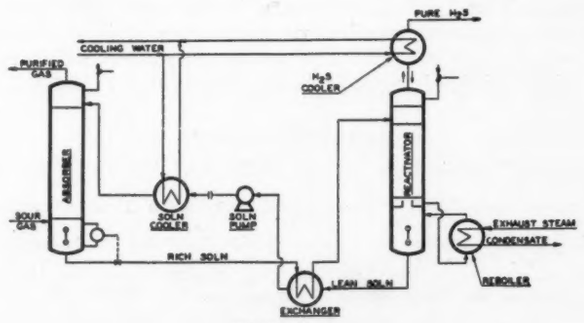


FIGURE 1
Flow Diagram of Girbotol Process.

A Girbotol absorbent is a single component. There is no exact pH* or acid-alkali balance to be maintained in the absorbing solution. This is important where there is a gradual accumulation of a fixed acid in the solution, as for example the accumulation of thiosulfuric acid in solutions scrubbing hydrogen sulfide from a gas containing traces of oxygen. The effectiveness of the available absorbent is not altered by partial neutralization of the solution or by variation in solution strength. There are no volatile components to pollute the purified gas. Plant-control tests are elementary.

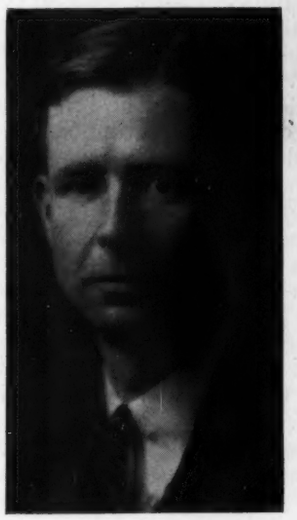
When the temperature of the amine solution is raised, its capacity for acid gas fall off rapidly, and a solution containing acid gas may be completely regenerated by bringing it to its boiling point. Regeneration can be accomplished by boiling the amine solution in a simple evaporator or pot still. However, the use of a column for regeneration is more economical, inasmuch as it reduces the steam consumption materially.

The reactivator in a Girbotol plant is primarily a unit of heat exchange. When a fixed gas such as hydrogen sulfide is driven from a water solution, it is saturated with steam at the temperature at which it leaves the solution. The lower this temperature,

* Hydrogen-ion concentration.

W. R. WOOD

W. R. Wood received his elementary education in the grade and high schools of Louisville, Kentucky, and was graduated by Cornell University in 1927. For two years he was engaged in technical work for E. I. du Pont de Nemours & Company at Newark, New Jersey. Employed by The Girdler Corporation in 1929, currently he is in the gas process division.



B. D. STORRS

B. D. Storrs, educated in the grade schools at Baltimore, Maryland, and the Baltimore Polytechnic Institute, was graduated in gas engineering by Johns Hopkins University in 1929. Employed by Standard Oil Company of New Jersey, he spent eight years in research, design and test work before joining the gas process division of The Girdler Corporation.

the smaller the amount of steam carried by the gas; and, inasmuch as heat must be supplied to the reboiler in proportion to that carried away by the steam, it is desirable to have the gas leaving the reactivator at a relatively low temperature. On the other hand, the top temperature of the tower cannot be too low, because heat must be supplied to bring the descending solution to its boiling point. A simple calculation shows that for each treating condition there is a noptimum feed-plate temperature to balance latent heat of effluent steam and sensible heat of amine solution. Because of the ease with which acidic gases are liberated from the amines due to the loose chemical bond, Girbotol reactivators are designed and operated with the proper temperature gradient down the tower for minimum heat consumption. This design and operation result in a considerable saving in heat and in cooling water, inasmuch as a heat balance on the plant shows that the cooling-water requirement is directly proportional to the heat supplied to the reboiler.

APPLICATION OF PROCESS

At the time of writing there are four Girbotol plants completed or under construction for removing hydrogen sulfide from refinery gases, and seven plants for purifying natural gas. There are also five Girbotol plants for scrubbing carbon dioxide from hydrogen produced by reacting hydrocarbon gas with steam. The hydrogen-sulfide plants are designed for a wide variety of treating conditions. Volumes vary from ½ million to 40 million cubic feet per day, pressures from 30 pound to 550 pound, temperatures from 50 to 160°F., and hydrogen-sulfide concentrations from 25 to 3000 grains per 100 standard cubic feet. In all Girbotol plants which have been placed in operation, the hydrogen-sulfide removal is better than 99 percent. The high efficiency of the process is best illustrated, however, by the fact that the carbon-dioxide content of industrial hydrogen is reduced from 18-20 percent to practically 0 in a single absorber of normal weight.

In some cases, particularly in the treatment of natural gas, it is desirable to remove not only the hydrogen sulfide, but also the water from the gas. This is accomplished by substituting a dehydrating agent for water in the Girbotol solution. Diethylene Glycol is the agent being used at the present time.

Dehydration prevents the formation of hydrocarbon hydrates in transmission lines and the attendant reduction in line capacity. A number of dehydrating processes are in use. Diethylene glycol has great affinity for water, and is one of the most satisfactory hygroscopic agents employed. It is non-corrosive and practically non-volatile, and stable at reactivation temperatures.

The Girbotol amines are completely miscible with diethylene glycol, and a mixture of these compounds removes both hydrogen sulfide and water from a gas stream. The operating cycle is identical with the usual Girbotol cycle, except that the reactivator is operated as a fractionating column to remove water from the glycol. The presence of evolved hydrogen sulfide in the reactivator assists in drying the glycol, so that the combination plant reduces the dew point of the treated gas to a lower temperature than is reached by diethylene glycol alone.

By controlling the ratio of diethylene glycol and water in the absorbing solution, the moisture content of the treated gas may be adjusted to any desired point from complete saturation to practically zero.

The hydrogenation of oils consumes large volumes of relatively pure hydrogen. This gas is generally produced by reforming and converting hydrocarbon gases to a mixture of hydrogen and carbon dioxide (18-20 percent) by the action of steam in the presence of a suitable catalyst, and then removing the carbon dioxide. The Girbotol process offers an economical means for reducing the carbon-dioxide content to practically zero in a cycle which is identical with the hydrogen-sulfide cycle. Separation with the amine solution is carried out at relatively low pressures, and the carbon dioxide is completely eliminated with small volumes of absorbing solution.

In hydrogenation plants where sulfur-free gas is not available, the Girbotol process serves two purposes. It removes hydrogen sulfide from the hydrocarbon gas used for the production of hydrogen to prevent catalyst poisoning, and it removes carbon dioxide from the finished hydrogen. Such a plant may be built as a combination unit consisting of two absorbers and a common reactivator.

Within the scope of this paper it is impossible to describe all of the applications of the Girbotol process. Other uses, such as the recovery of carbon dioxide in dry-ice plants, the recovery of hydrogen sulfide, the purification of gas-engine fuel, and the production of inert atmospheres, have not been discussed. The Girbotol process is a simple, unusually efficient process, applicable whenever it is desirable to remove or recover acid gases from gas mixtures. Its field of usefulness is being constantly expanded.

BIBLIOGRAPHY

Bottoms, "Organic Bases for Gas Purification," *Ind. Eng. Chem.* **23**, 501 (1931).

Bottoms and Wood, "The Girbotol Purification Process," *Refiner Natural Gasoline Mfr.* **14**, 105 (1935):

Gregory and Scharmann, "Carbon-Dioxide Scrubbing by Amine Solutions," *Ind. Eng. Chem.* **29**, 514 (1937).

Mason and Dodge, "Equilibrium Absorption of Carbon Dioxide by Solutions of the Ethanolamines," *Trans. Am. Inst. Chem. Eng.* **32**, 1 (1935).

Gas Purification

By the I. G. Alkacid Process and

Sulfur Recovery

By the I. G. Claus Process

HANS BAEHR

I. G. Farbenindustrie A.-G.,
Ludgwigshafen am Rhein, Germany

THE use of alkaline inorganic scrubbing agents, such as sodium- or potassium-carbonate solutions, for the absorption of weak acids such as carbon dioxide or hydrogen sulfide from gases, has not been found economical due to the low absorptive capacity of these solutions for hydrogen sulfide and carbon dioxide. The absorption of these gases was improved by the use of aqueous solutions of tripotassium phosphate and the slightly-volatile organic bases of the alkylolamine group such as mono-, di-, and triethanolamine used in the Girdler process.

In the Alkacid process, strong inorganic bases with weak organic non-volatile acids, such as aminosulfoacids and aminocarbonicacids, are used as the absorption agents. Three solutions were developed and introduced in the market under the names Alkacid solution "M," Alkacid solution "Dik," and Alkacid solution "S"—each of which has a specific field of application. Alkacid solution "M" is used for the removal of hydrogen sulfide or carbon dioxide, either separately or simultaneously. Alkacid solution "Dik" is used for the selective removal of hydrogen sulfide from gases containing carbon dioxide, and Alkacid solution "S" is used for removing hydrogen sulfide and carbon dioxide from gases containing impurities such as tar, dust, and certain other gas constituents. A much shorter time of contact is required for the saturation of these Alkacid solutions than for the other solutions mentioned.

The selectivity of the Alkacid solutions depends not only on the chemical composition, but also on the physical conditions employed, such as the time of contact, the temperature, etc. The absorption takes place at a low temperature, while the reactivation is carried out at 105° C.

The weak acids, such as hydrogen sulfide and carbon dioxide, and also ammonia separated by the Alkacid process can be worked up into various products. In this connection, particular reference has been made to the processing of hydrogen sulfide by the "improved I. G. Claus process" for the production of sulfur. In this process, most of the heat of reaction is removed by cooling during the combustion of the hydrogen sulfide by the generation of steam in a boiler. The conversion of the gas containing hydrogen sulfide and sulfur dioxide then takes place, producing free sulfur. The ammonium-sulfide solution, obtained from the scrubbing of ammonia and hydrogen sulfide, can be converted into ammonium sulfate.

A number of Alkacid plants for the removal of hydrogen sulfide and carbon dioxide are operating in Germany and other countries at the present time, and 12 plants are under construction. The amount of hydrogen sulfide removed from gases by the Alkacid process already corresponds to more than 30,000 metric tons per year of sulfur, which indicates the technical development of this process.

This paper was presented at Eighth Mid-Year Meeting, American Petroleum Institute, Wichita, Kansas, May 24, 1938.

IMPURITIES of a slightly acid nature, such as hydrogen sulfide, carbon dioxide, and hydrocyanic acid, have been removed from gases by the use of such basic substances as lime,[1] alkali hydroxides, and especially sodium- or potassium-carbonate solutions,[2, 3] as these solutions can be readily regenerated.

The absorptive powers of the latter solutions are low, and an attempt was made to find more efficient, easily-regenerated solutions for the removal of hydrogen sulfide and carbon dioxide. Rosenstein[4] states that solutions of tribasic sodium phosphate absorb considerable quantities of hydrogen sulfide at low temperatures, and on heating the solution the gas is liberated.

Bottoms,[5] of the Girdler Corporation, found that the alkylol amines, especially mono-, di- and triethanolamine, and later diaminopropanol, absorb hydrogen sulfide and carbon dioxide. These amines are strong organic bases and water-soluble substances which readily absorb hydrogen sulfide and carbon dioxide at low temperatures, and then liberate these gases when heated to 100° C. The following reactions for these processes are assumed by Bottoms:

$$2RNH_2 + H_2S \underset{100^\circ\ C.}{\overset{20^\circ\ C.}{\rightleftharpoons}} (RNH_3)_2H_2S$$

$$2RNH_2 + CO_2 + H_2O \underset{100^\circ\ C.}{\overset{20^\circ\ C.}{\rightleftharpoons}} (RNH_3)_2H_2CO_3$$

These bases absorb several times as much hydrogen sulfide and carbon dioxide per unit volume as do the sodium- and potassium-carbonate solutions. As the main expense in the regeneration process is incurred

by the cost of heating the used solution, the most economical solutions are those showing the greatest absorptive capacity for the weak acids. The discovery of these organic bases represents great progress towards the solving of the problem. These substances offer a certain disadvantage, however; for, even though they are only slightly volatile, small quantities of them are entrained with the purified gas and with the expelled steam, and in a continuous cycle these losses become appreciable with prolonged operation. Several plants in the United States are being operated successfully according to this process for the removal of hydrogen sulfide and carbon dioxide.

ALKACID PROCESS

I. REQUIREMENTS FOR SCRUBBING SOLUTIONS

On the assumption that strong inorganic or organic bases in combination with slightly-volatile organic acids should represent solutions which make the absorption of weak acids at low temperatures and their liberation at high temperatures possible, the alkali salts of weak organic acids, with dissociation constants similar to those of hydrogen sulfide and carbon dioxide, were investigated. Aqueous solutions of alkali salts of the amino acids were found to be effective solutions.[6] The following reactions have been assumed for this process:

$$2RCOONa + H_2S \rightleftharpoons 2RCOOH + Na_2S$$
$$RCOONa + H_2S \rightleftharpoons RCOOH + NaSH$$
$$RCOONa + NH_3 + H_2S \rightleftharpoons RCOONH_4 + NaSH$$
$$2RCOONa + 2NH_3 + H_2S \rightleftharpoons 2RCOONH_4 + Na_2S$$

The formation of free organic weak acids, alkali sulfide, and hydrosulfide can be assumed when weak acids like hydrogen sulfide are absorbed. Upon heating, the weak organic acid reacts with the alkali sulfides or hydrosulfides in the solution forming the alkali salts of the weak organic acids and liberating the hydrogen sulfide. The reactions are similar in the case of carbon dioxide.

There are numerous organic weak acids which react in the way described, but investigations were made to find solutions of high efficiency—which is dependent on the absorptive power of the weak acids in the solution, and on the ease of separating the absorbed gases by heating. For use on a plant scale, the solutions, furthermore, must be stable; and the impurities contained in the gas, such as tar, dust, hydrocyanic acid, and oxygen, must not retard the efficiency. The volatility of the scrubbing solution must be low, as the solution must not escape with the purified gas or with the liberated impurities.

II. PROPERTIES OF ALKACID SOLUTIONS

During the course of this work, three solutions were developed to meet the requirements mentioned above. These solutions, which differ in their absorptive capacity for hydrogen sulfide and carbon dioxide, are known as Alkacid solutions,[7] "M," "Dik," and "S"; and are used in accordance with the required removal of these impurities. Alkacid solution "M" is used for the removal of either gas, when present alone, or for removal of both gases simultaneously. Alkacid solution "Dik" is used for the selective removal of hydrogen sulfide from gases containing carbon dioxide, and also from gases containing small quantities of carbon disulfide and hydrocyanic acid. Alkacid solution "S" is used for the same purpose as either solution "M" or "Dik" when the gas contains an appreciable amount of other impurities, such as hydrocyanic acid, ammonia, carbon disulfide, mercaptans, dust, and tar.

III. EXAMINATION OF SCRUBBING SOLUTIONS

In order to evaluate the absorptive capacity of the scrubbing solution for weak acids, the absorption value must be determined. This is obtained by shaking approximately 10 ml. of the solution with carbon dioxide for 2 minutes; and the carbon dioxide absorbed in this time, calculated on the basis of 1 ml. of solution, gives the absorption value which indicates the absorptive capacity that can be expected in practical operation.

The saturation value, by means of which any changes in the solution can be determined over a long period of operation, is obtained from the above solution after carbon-dioxide treatment. The solution is decomposed with sulfuric acid, and the carbon dioxide released is collected in a Scheibler volume meter. The quantity of carbon dioxide obtained, calculated on the basis of 1 ml. of solution, is the saturation value.

If the reactivated solution is decomposed by an excess of sulfuric acid, and the carbon dioxide is collected in a volume meter, the amount of carbon dioxide will give the blank or reactivation value. This value represents the quantity of carbon dioxide that is present in the solution after regeneration, and this serves to control the regenerating columns in practical operation. A similar procedure can be used in the case of hydrogen-sulfide removal.

The absorption rate plays an important role in determining the practical value of the solution. The absorptive capacity of different solutions for carbon dioxide, with varying times of contact, is shown in Figure 1. The curves indicate that the Alkacid solution becomes saturated in a few minutes, while the soda and potash solutions require a much longer time of contact for saturation. On this basis, the scrubbing effect of the Alkacid solution is much better than the soda and potash solutions; and, in general, the absorption rate during the first 2 minutes of contact determines the effectiveness of the solution.

IV. EFFECT OF VARIOUS CONDITIONS ON THE SELECTIVITY OF ALKACID SOLUTIONS

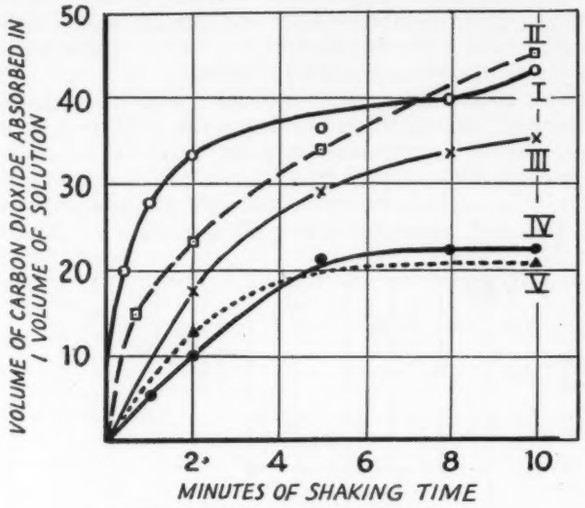
a. *Effect of Chemical Composition of the Solutions*

As shown above, the absorption value of the solution with carbon dioxide in unit time can be used to evaluate the solutions. Certain solutions, however, act differently with hydrogen sulfide and carbon dioxide, as shown in Figure 2. The saturation value of Alkacid "M," with respect to hydrogen sulfide and carbon dioxide, is reached in a comparatively short time; while Alkacid "Dik" solution becomes saturated with hydrogen sulfide in a very short time, and a much longer time is required for saturation with carbon dioxide. These curves indicate the selectivity of the Alkacid "M" and "Dik" solutions for hydrogen sulfide and carbon dioxide, and these properties determine their use in practice.

b. *Effect of Time of Contact*

The selectivity of the scrubbing process for the absorption of hydrogen sulfide and carbon dioxide is also dependent on the type of equipment used. Buetefisch[7] pointed out that the absorption rate of carbon dioxide in water or alkaline solutions is very slow, due to a hydration which must precede the absorption, while hydrogen sulfide is absorbed very rapidly. In view of this, the scrubbing towers for the removal

of hydrogen sulfide can be smaller than those to be used for carbon-dioxide removal. Furthermore, scrubbing gases containing both hydrogen sulfide and carbon dioxide at high velocities will remove chiefly hydrogen sulfide with little carbon dioxide.



I. Alkacid "M."
II. Triethanolamine, 50-percent solution.
III. Potassium carbonate, 30-percent solution.
IV. Tripotassium phosphate, 22-percent solution.
V. Sodium carbonate, 10-percent solution.

FIGURE 1
Absorption Capacity of Various Scrubbing Solutions.

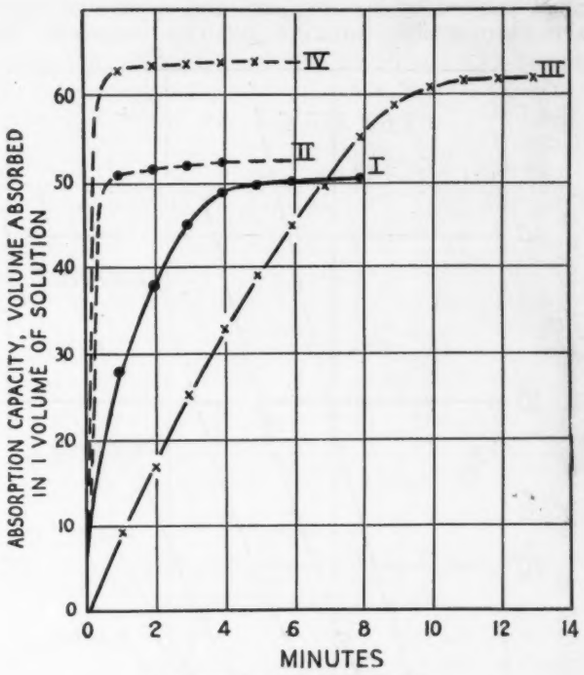
c. *Effect of Temperature*

The temperature also influences the absorption rate of hydrogen sulfide and carbon dioxide; for, while hydrogen sulfide is absorbed rapidly both at low and at high temperatures, the rate of absorption of carbon dioxide increases with rise in temperature. The optimum temperature in the latter, however, is dependent on the fact that the partial pressure of carbon dioxide of the absorbing solution also increases with rise in temperature. The absorptive capacity will be less than at a lower temperature, due to the higher partial pressure of carbon dioxide in the solution. These conditions are similar for all alkaline absorption solutions, and a comparison of the partial pressures of carbon dioxide at various temperatures for Alkacid and Girdler solutions is shown in Figure 3. The curves indicate the extent of carbon-dioxide removal from the gas at the respective temperatures and degree of regeneration of the solution. In practice, the hydrogen sulfide should be absorbed at as low a temperature as possible, and carbon dioxide at a higher temperature. In the case of carbon dioxide it might be desirable to remove the major part at higher temperatures, and the remaining at lower temperatures.

The same conditions prevail when employing vacuum or pressure operation. When working under pressure, approximately the same partial pressure of carbon dioxide and hydrogen sulfide is reached as at normal pressure; and, after releasing the pressure, the carbon-dioxide and hydrogen-sulfide content of the gas is lower than in the absorption under normal pressure in proportion to the pressure applied.

V. REGENERATION OF THE SOLUTION

The carbon dioxide and hydrogen sulfide absorbed by the solution at low temperatures are liberated by heating. The evolution of the gas starts at approximately 90° C., but this depends, to a great extent, upon the amount of gas absorbed by the solution; for the more nearly saturated the solution, the lower the temperature required for initial gas evolution. The most effective evolution of gas is obtained at a temperature of approximately 105° C. The rate of reactivation is influenced, to a great extent, by the use of packing in the regenerating tank, as shown graphically in Figure 4. A small quantity of carbon dioxide or hydrogen sulfide remains in the solution after reactivation, which has no appreciable effect on the scrubbing process; while if the gases were completely removed from the solution, the steam consumption would be high—and this would make the process unnecessarily expensive. The extent of reactivation of the solution, the blank or reactivation value, is determined as explained under (III) above.



I. Alkacid "M"—carbon dioxide.
II. Alkacid "M"—hydrogen sulfide.
III. Alkacid "Dik"—carbon dioxide.
IV. Alkacid "Dik"—hydrogen sulfide.

FIGURE 2
Difference in the Selectivity of Alkacid Solution "M" and "Dik" Solution in Absorbing Carbon Dioxide and Hydrogen Sulfide.

VI. EFFECT OF VARIOUS GAS CONSTITUENTS

a. *Gas Impurities*

In many gases there are, in addition to hydrogen sulfide and carbon dioxide, impurities such as hydrocyanic acid, mercaptans, carbonoxysulfide, and carbon disulfide—the first three of which have no effect on the Alkacid solutions; carbon disulfide, however, has an effect on only Alkacid solution "Dik." If there are impurities in the gas such as dust, tar, phenols, etc., which gradually consume alkali in the solution, it is necessary to purify the gas by pre-treatment with an alkaline or ammoniacal solution.

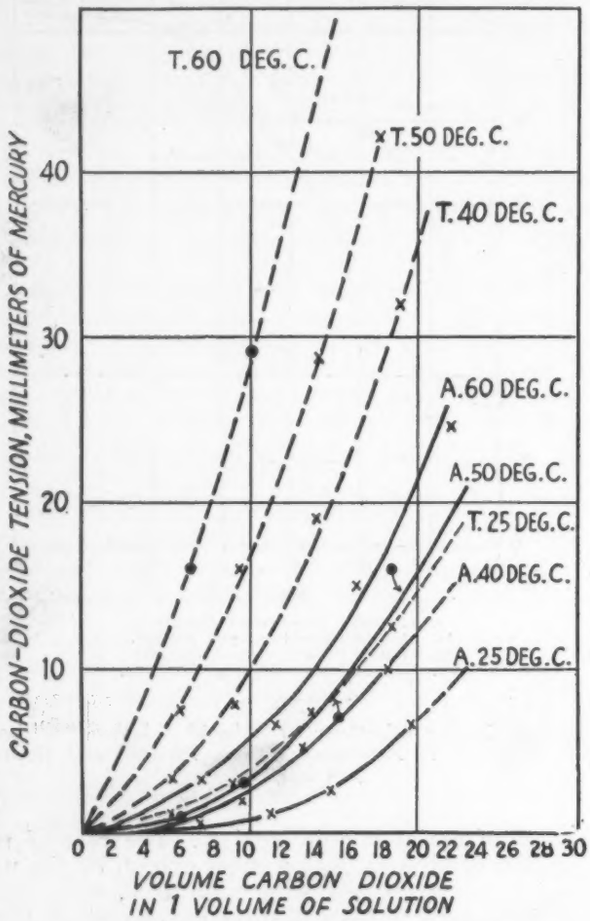
b. *Simultaneous Removal of Ammonia and Hydrogen Sulfide*

Many gases, such as those obtained from coke ovens, or from the distillation of brown coal, contain ammonia, which can be scrubbed out with the hydrogen sulfide and/or carbon dioxide by the Alkacid

solutions. For the case of ammonia and hydrogen sulfide, the following reactions take place:

$$RCOONa + NH_3 + H_2S \rightleftharpoons RCOONH_4 + NaSH$$
$$2RCOONa + 2NH_3 + H_2S \rightleftharpoons 2RCOONH_4 + Na_2S$$

The hydrogen sulfide and ammonia are absorbed and then liberated by reactivation, and separated out as ammonium-sulfide solution by condensation. This


T. 60 DEG. C.
T. 50 DEG. C.
T. 40 DEG. C.
A. 60 DEG. C.
A. 50 DEG. C.
T. 25 DEG. C.
A. 40 DEG. C.
A. 25 DEG. C.
CARBON-DIOXIDE TENSION, MILLIMETERS OF MERCURY
VOLUME CARBON DIOXIDE IN 1 VOLUME OF SOLUTION
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
10
20
30
40

T = 50 percent by volume of triethanolamine.
A = Alkacid "M"—35 percent.

FIGURE 3

Effect of Temperature, in Degrees C., and Carbon-Dioxide Content on Partial Pressures of Scrubbing Solution for Carbon Dioxide.

ammonium-sulfide solution can then be processed into other products.

VII. TECHNICAL ASPECTS OF THE ALKACID PROCESS

a. *General Procedure*

The general scheme of this process is very simple. The equipment consists essentially of a scrubbing tower, a stripping column, a heat exchanger and cooler. A flow diagram of the process is shown in Figure 5. The gas to be purified is scrubbed in the absorber tower countercurrently with cold reactivated Alkacid solution, which absorbs the hydrogen sulfide and carbon dioxide from the gas, and collects in the lower section of the tower as a saturated solution. The solution is then pumped through the heat exchanger, in which it is heated to 80-90° C., and then enters the top of the reactivating column. The gas is stripped of its absorbed constituents by steam generated by a re-boiler, and the hot reactivated solution is withdrawn from the bottom of the tower, cooled to 40-50° C. by heat exchange with the used solution from the absorber tower. The solution, after further cooling in a water cooler, enters the top of the scrubbing tower. The process is continuous, and the only utility requirements are steam, water, and power.

The Alkacid solutions are relatively non-corrosive, and the equipment requires no special materials of construction with the exception of a few parts which are particularly subjected to wear.

After condensing the steam, the carbon dioxide and hydrogen sulfide liberated from the reactivator are available for any desired purpose. For the removal of both carbon dioxide and hydrogen sulfide from a gas without separate recovery, a single scrubbing tower can be used, provided that sufficient time of contact

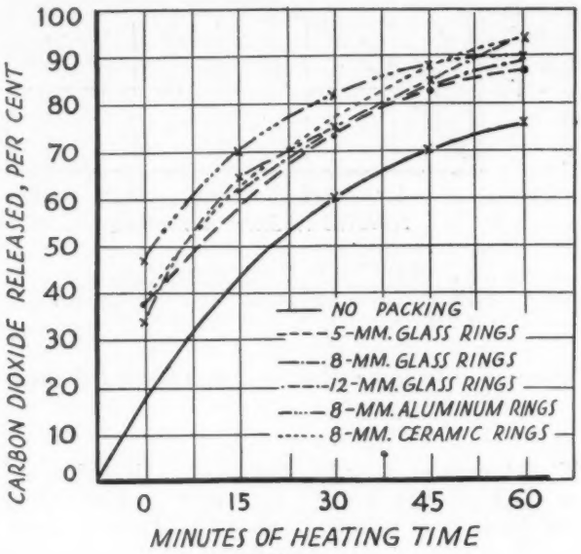

CARBON DIOXIDE RELEASED, PER CENT
MINUTES OF HEATING TIME
NO PACKING
5-MM. GLASS RINGS
8-MM. GLASS RINGS
12-MM. GLASS RINGS
8-MM. ALUMINUM RINGS
8-MM. CERAMIC RINGS
0 15 30 45 60
0 10 20 30 40 50 60 70 80 90 100

FIGURE 4

Reactivation of Saturated Alkacid Solution.

for the removal of the carbon dioxide is obtained. If hydrogen sulfide alone is to be removed from gas containing carbon dioxide, Alkacid solution "Dik" should be used—allowing a short time of contact in the absorber tower.

For the removal of both hydrogen sulfide and carbon dioxide from the gas, and for their separate recovery, the hydrogen sulfide and carbon dioxide can either be removed separately; or they can be scrubbed out together, and then the hydrogen sulfide removed from the carbon dioxide by means of the selective Alkacid solution "Dik." This solution will give hydrogen sulfide of 50-60 percent purity from a gas mixture consisting of five parts of hydrogen sulfide and 95 parts of carbon dioxide.

b. *Simultaneous Removal of Ammonia and Hydrogen Sulfide, and Recovery of Ammonium-Sulfide Solution*

The most important class of gases containing ammonia is that of the distillation gases obtained from bituminous coal in coke and gas plants for the production of illuminating gas. These gases contain approximately 0.17-0.23 gram of ammonia, 0.17-0.34 gram of hydrogen sulfide, and 0.03 gram of hydrocyanic acid, per cubic foot. The gases from the coke ovens are cooled; and the water vapor, tar, and part of the ammonia, are separated. The so-called gas-liquor is then separated from the tar; and ammonia, hydrogen sulfide, and carbon dioxide are stripped out. The vapors containing ammonia, hydrogen sulfide, and carbon dioxide are returned to the unpurified gas stream before the cooler. The gas containing the total

amount of ammonia and hydrogen sulfide is cooled, and then enters the Alkacid plant—the details of which are shown in Figure 6.

The sour gas enters at the bottom of the absorber tower, and the purified gas leaves at the top. In the lower section of the tower, the spent solution is recycled in order to saturate the solution with the carbon dioxide and hydrogen sulfide contained in the gas. The weak organic acids of the Alkacid "S" solution separate out, and are then withdrawn and returned to the main cycle of the solution; while the spent solution, which consists chiefly of alkali-rhodanate and alkali thiosulfate, is removed. Alkali hydroxide or carbonate is added to the main solution, to replace the alkali removed with the rhodanate and thiosulfate.

In the center section of the tower, the gas is scrubbed with the reactivated solution, whereby the ammonia, hydrogen sulfide, and small amounts of hydrocyanic acid and carbon dioxide are absorbed by the solution. The solution saturated with ammonia and hydrogen sulfide is removed from the lower part of the central section of the tower, and then pre-heated in a heat exchanger and pumped to the top of the reactivator tower, in which tower the ammonia and hydrogen sulfide are stripped from the gas by a steam re-boiler. The ammonia and hydrogen sulfide, together with steam, are withdrawn from the top of the column. A portion of the vapors is condensed, and the condensate is returned to the tower, while the remaining vapors are condensed to ammonium-sulfide solution. The concentration of the ammonia in the ammonium-sulfide solution can be controlled by regulating the temperature in the first cooler. The regenerated solution is withdrawn from the bottom of the tower, and returned through the heat exchanger and cooler to the top of the absorber tower.

VIII. REMOVAL OF HYDROGEN SULFIDE FROM LIQUIDS SUCH AS GASOLINE, BENZOL, ETC.

Weak acids such as hydrogen sulfide are frequently present in gasoline and oil, and they must be removed. The Alkacid process can be used in this case by extraction of the liquids with Alkacid solution, or

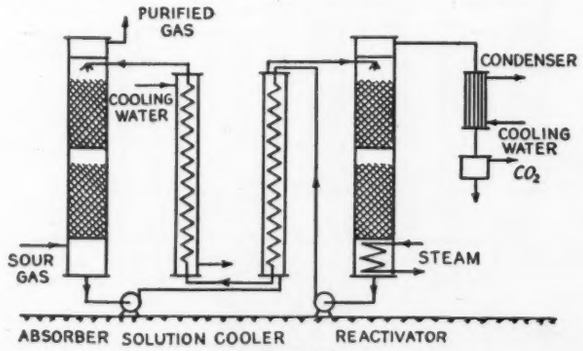


FIGURE 5

Flow Diagram of Alkacid Process for the Purification of Gases from Carbon Dioxide.

by stripping the acid gases by introducing an inert gas into the liquid and subsequently absorbing the hydrogen sulfide liberated in the Alkacid solution. In the case of highly-volatile liquids such as gasoline, the inert gas stream, after treatment with Alkacid solution, is re-cycled for further stripping. It is, therefore, possible to minimize losses of low-boiling liquids.

The process of removing hydrogen sulfide from gasoline consists of passing the gasoline down through the scrubber and treating countercurrently with a gas stream, such as nitrogen, carbon dioxide, etc., whereby the hydrogen sulfide in the gasoline is removed. The hydrogen sulfide taken up by the inert gas is treated with Alkacid solution in an absorber, and then the solution saturated with hydrogen sulfide is regenerated as described above. The purified

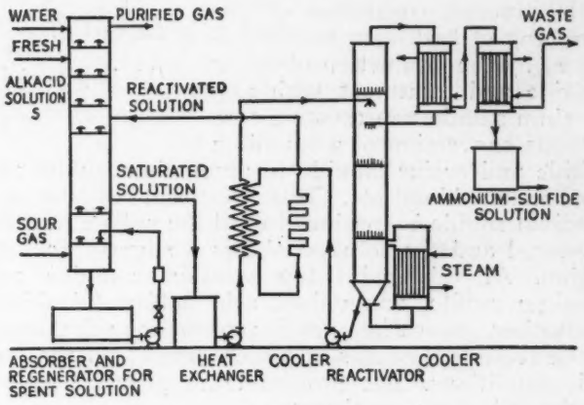


FIGURE 6

Separation of Ammonia and Hydrogen Sulfide from Distillation Gases by the Alkacid Process with Recovery of Ammonium-Sulfide Solution.

gas from the absorber, containing a small amount of gasoline, is re-cycled to the first tower for further sulfurization of gasoline.

IX. PROCESSING OF THE ACID CONSTITUENTS REMOVED BY THE ALKACID PROCESS

a. *Carbon Dioxide*

The carbon dioxide separated in the Alkacid plant leaves the stripper mixed with steam, and may be released directly into the atmosphere if no further processing is contemplated. The gas may be utilized for various purposes; e. g., in the manufacture of dry ice. The carbon dioxide as produced by the Alkacid process is favorable for this use, inasmuch as it contains no entrained particles to impair its flavor.

b. *Hydrogen Sulfide*

The hydrogen sulfide may be used for various purposes, such as in the production of sulfur, sulfuric acid, sulfites, sulfates, etc. Hydrogen sulfide, by reaction with air or oxygen, can be converted into sulfur dioxide, which may be converted into sulfites by the use of alkalies, or may be oxidized to sulfur trioxide or sulfuric acid in the presence of catalysts. Whereas the processing of hydrogen sulfide to free sulfur is of interest in countries where sulfur consumption is high and sulfur resources low, the manufacture of sulfuric acid becomes of importance in oil refining; for the acid produced from the hydrogen sulfide recovered from the cracked gas may be utilized directly for the purification of gasoline.

The processing of hydrogen sulfide derived from coke-oven distillation gases is somewhat different; for the hydrogen sulfide may be combined with the ammonia contained in these gases. This may be accomplished either by the production of sulfites from the ammonia and the hydrogen sulfide, followed by the conversion to sulfate, or by the production of sulfuric acid from the hydrogen sulfide and reaction

ot the ammonia with sulfuric acid to ammonium sulfate.

The production of ammonium sulfate from ammonium sulfide takes place according to the following process: Hydrogen sulfide is burned with oxygen or oxygen-containing gases to sulfurous acid. This is contacted with the ammonium sulfide in solution or in vapor phase. The ammonia combines with the sulfurous acid, and the hydrogen sulfide is released and converted into sulfur dioxide by combustion. This process, consisting of the stripping of hydrogen sulfide followed by the production of sulfur dioxide and treatment with ammonium sulfide, represents a continuous conversion of ammonium sulfide and sulfur dioxide to ammonium sulfite and ammonium thiosulfate. This treatment of the ammonium sulfide is continued until the sulfide has disappeared and the solution shows a slightly acid reaction. At this point the solution contains ammonium sulfite, ammonium acid sulfite (bisulfite), ammonium thiosulfate, and ammonium polythionate —the relative amounts of which depend on the specific conditions. The process takes place according to the following reactions:

$$H_2S + 1\frac{1}{2}O_2 \longrightarrow SO_2 + H_2O + 124 \text{ Kg.-Cal.*}$$
$$(NH_4)_2S + SO_2 + H_2O \longrightarrow (NH_4)_2SO_3 + H_2S$$
$$(NH_4)_2S + 2SO_2 + 2H_2O \longrightarrow 2NH_4HSO_3 + H_2S$$
$$6NH_4HSO_3 + 2(NH_4)_2S \longrightarrow 2(NH_4)_2SO_3 + 3(NH_4)_2S_2O_3 + 3H_2O$$

*Kilogram calory.

The solutions containing ammonium sulfite and bisulfite can be converted into ammonium sulfate and sulfur[8] by heating at atmospheric or higher pressure. If the acid content of the solution is not sufficient for sulfate formation, the proper acidity may be obtained by the addition of sulfurous acid, or mineral acids such as sulfuric acid—particularly waste acid from benzol or oil refining. The conversion to ammonium sulfate takes place according to the following reactions:

$$(NH_4)_2SO_3 + 2NH_4HSO_3 \longrightarrow 2(NH_4)_2SO_4 + S + H_2O$$
$$(NH_4)_2S_2O_3 + 2NH_4HSO_3 \longrightarrow 2(NH_4)_2SO_4 + 2S + 2H_2O$$

This procedure is particularly advantageous; for it is possible to utilize the intermediate solution, consisting of ammonium sulfite and bisulfite for the final purification of the gas which is to be used for illuminating purposes. The purification is done after the gas has been compressed to pipe-line pressure, and after the solution has served its purpose it can be converted into ammonium sulfate.

X. THE IMPROVED I.G. CLAUS PROCESS

a. *Chemical Assumptions*

As pointed out above, the hydrogen sulfide released by the Alkacid process can be converted into free sulfur by combustion with air. Generally, a conversion of only 2 cubic feet to 3 cubic feet of hydrogen sulfide per hour per cubic foot of catalyst can be obtained, due to the large amount of heat produced. The heat generated by combustion must be removed by radiation, in order that the proper reaction temperature for conversion to sulfur is not exceeded. The removal of heat by use of cooling pipes arranged in the top of the Claus oven did not give any increased efficiency.

The Claus process was changed in such a way that, in the first step, part of the hydrogen sulfide with air, or oxygen-containing gases, is converted into sulfurous acid while utilizing the heat evolved for the generation of steam. In the second step, the reaction mixture is passed over the catalyst, transforming the hydrogen sulfide and sulfurous acid into sulfur. The mechanism of hydrogen-sulfide conversion, according to the old Claus process and the improved I. G. Claus process, is indicated by the following reactions:

(a) Old Claus Process

$$3H_2S + 1\frac{1}{2}O_2 \longrightarrow 3S + 2H_2O + 159 \text{ Kg.-Cal. in the catalyst}$$

(b) Improved I. G. Process

$$H_2S + 1\frac{1}{2}O \longrightarrow SO_2 + H_2O + 124\text{-}138 \text{ Kg.-Cal. in the boiler}$$
$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O + 21\text{-}35 \text{ Kg.-Cal. in the catalyst}$$

In the old Claus process the heat of reaction, 53 Kg.-Cal. per mol of hydrogen sulfide, had to be removed by radiation; while in the I. G. Claus process 41-46 Kg.-Cal., depending on the temperature of the gas, are removed by the cooling equipment, so that only 7-12 Kg.-Cal. are liberated in the actual contact process. This is accomplished by using 1 cubic foot of a suitable catalyst, with which 200 to 300 times the quantity of hydrogen sulfide can be converted per hour; and this is a great improvement over the old process.

Removal of the heat can be accomplished in many ways, and by various agents such as air, gas, and water; but it is desirable to remove the heat in a steam boiler.

b. *Development of the Process*

A flow diagram of the process is shown in Figure 7; and the equipment consisting of an apparatus for removing the heat, such as a boiler, a Claus oven, and a sulfur separator, is connected to an Alkacid plant. The gases from the Alkacid plant are burned with the necessary amount of air in the boiler to which the heat evolved is released. The gases at 250 to 300° C. are passed over the catalyst, and the final conversion takes place; sulfur separates out in liquid form partly in the sump of the oven and partly in the centrifugal separator.

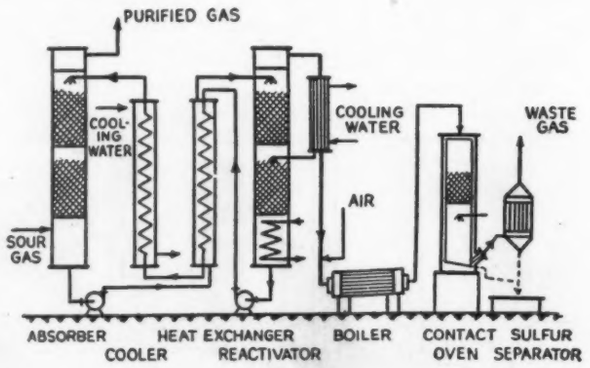
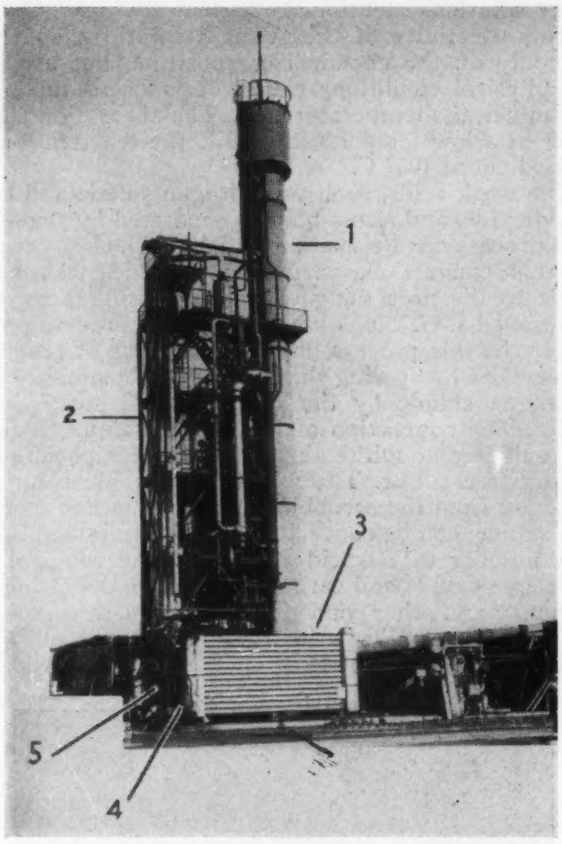


FIGURE 7

Flow Diagram of Alkacid Process for the Purification of Gases from Hydrogen Sulfide and Recovery of Hydrogen Sulfide as Free Sulfur.

A 92- to 94-percent yield is obtained, based on the hydrogen sulfide fed to the plant. The hydrogen sulfide and sulfur dioxide remaining in the gas can be completely converted into sulfur with water or aqueous salt solutions. The hydrogen sulfide can also be

catalytically converted into sulfur dioxide with air, and the sulfur dioxide may be further processed to sulfuric acid.



1. Scrubbing tower.
2. Reactivator.
3. Heat exchanger.
4. Vapor cooler.
5. Operating stall.

FIGURE 8
An Alkacid Plant Installation.

XI. APPLICATION OF THE ALKACID PROCESS

The application of the Alkacid process has grown considerably since its development. At the present time around 150,000,000 cubic feet per day of gas are being purified by this process in Germany, and approximately 1,000,000 cubic feet per day of hydrogen sulfide are separated. The process has been in operation for a number of years in two gasoline plants for the purification of water gas and hydrogenation waste gases. A large plant for the purification of carbon dioxide from gases produced by the catalytic reaction of carbon monoxide with steam is in operation outside of Germany; and a number of additional plants for the removal of hydrogen sulfide and carbon dioxide in the synthesis of gasoline and oil have been put into operation recently in Germany and other countries, and 12 plants are under construction at the present time.

Close to 30,000 metric tons per year of sulfur are obtained from the operation of the Alkacid process in Germany, and this represents more than half of the German sulfur production.

An Alkacid plant installation for processing 530,000 cubic feet per hour of gas containing 0.42 gram hydrogen sulfide per cubic foot is shown in Figure 8. This illustration will give an idea of the construction and size of such a plant, and the various sections are designated by the figures shown as follows:

(1) Scrubbing tower; (2) reactivator; (3) heat exchanger; (4) vapor cooler; (5) operating stall. The control of operation is centralized in the operating stall, and one man is required. In the above plant the hydrogen sulfide in the gas is reduced from 42 grams to 2 grams per 100 cubic feet, with the following water and steam consumption:

Solution circulation rate	3,170 gal. per hour
Steam (1 lb. per gal. solution circulation)	3,170 lb. per hour
Water (winter)	6,350 gal. per hour
(summer)	9,525 gal. per hour

Figures 9 to 11, inclusive, illustrate the improved

1 and 2—Claus ovens.
3 and 4—Boilers.
5—Sulfur separator.

FIGURE 9
Improved I. G. Claus Process.

I. G. Claus process. Two Clause ovens (**1** and **2**) are shown with the necessary boilers (**3** and **4**), and the sulfur separator (**5**) is constructed as a centrifugal separator. Each plant unit produces 40 metric tons per day of sulfur, which runs off in liquid form from the bottom of the Claus oven and centrifugal separator, and is molded into cubes, etc., in a suitable apparatus, as shown in Figure 11.

1. Claus oven.
3. Boiler.

FIGURE 10
Improved I. G. Claus Process.

SUMMARY

The use of alkaline inorganic scrubbing agents, such as sodium- or potassium-carbonate solutions, for the absorption of weak acids such as carbon dioxide or hydrogen sulfide from gases, has not been found economical due to the low absorptive capacity of these solutions for hydrogen sulfide and carbon dioxide. The absorption of these gases was improved by the use of aqueous solutions of tripotassium phosphate and the slightly-volatile organic bases of the alkylolamine group such as mono-, di-, and triethanolamine used in the Girdler process.

In the Alkacid process, strong inorganic bases with weak organic non-volatile acids, such as aminosulfoacids and aminocarbonicacids, are used as the absorption agents. Three solutions were developed and introduced in the market under the names Alkacid solution "M," Alkacid solution "Dik," and Alkacid solution "S"—each of which has a specific field of application. Alkacid solution "M" is used for the removal of hydrogen sulfide or carbon dioxide, either separately or simultaneously. Alkacid solution "Dik" is used for the selective removal of hydrogen sulfide from gases containing carbon dioxide, and Alkacid solution "S" is used for removing hydrogen sulfide and carbon dioxide from gases containing impurities such as tar, dust, and certain other gas constituents. A much shorter time of contact is required for the saturation of these Alkacid solutions than for the other solutions mentioned.

The selectivity of the Alkacid solutions depends not only on the chemical composition, but also on the physical conditions employed, such as the time of contact, the temperature, etc. The absorption takes place at a low temperature, while the reactivation is carried out at 105° C.

The weak acids, such as hydrogen sulfide and carbon dioxide, and also ammonia separated by the Alkacid process can be worked up into various products. In this connection, particular reference has been made to the processing of hydrogen sulfide by the "improved I. G. Claus process" for the production of sulfur. In this process, most of the heat of reaction is removed by cooling during the combustion of the hydrogen sulfide by the generation of steam in a boiler. The conversion of the gas containing hydrogen sulfide and sulfur dioxide then takes place, producing free sulfur. The ammonium-sulfide solution, obtained from the scrubbing of ammonia and hydrogen sulfide, can be converted into ammonium sulfate.

A number of Alkacid plants for the removal of hydrogen sulfide and carbon dioxide are operating in Germany and other countries at the present time, and 12 plants are under construction. The amount of hydrogen sulfide removed from gases by the Alkacid process already corresponds to more than 30,000 metric tons per year of sulfur, which indicates the technical development of this process.

FIGURE 11
Improved I. G. Claus Process.

BIBLIOGRAPHY

[1] Philips, English Patent 4142 (1817).
[2] Espenhahn and Koppers Co., Pittsburgh, U. S. Patent 1,440,977; Hultman, English Patent 436,218.
[3] Petit, German Patent 471,042, 396,353, 502,908, 539,733; Lorenzen, *Z. angew. Chemie*, **42**, 768 (1929); Muhlert, *Kohlenschwefel*, 96.
[4] Rosenstein, U. S. Patent 1,945,163; *Petroleum*, **24** [**24**] 4-6.
[5] Bottoms, German Patent 549,556, 606,162; U. S. Patent 1,783,901; *Z. angew. Chemie*, **44**, 902 (1931); Thau, *Gas und Wasserfach*, **74**, 1152 (1931); Bottoms and Wood, *Refiner Natural Gasoline Mfr.* **14**, 35 and 105 (1935).
[6] I. G. Farbenindustrie, French Patent 738,747, 738,814.
[7] Buetefisch, *Chem. Fabrik*, **8**, 228 (1935).
[8] Baehr, *Glueckauf*, **73**, 901 (1937); Chem. Fabrik, **11**, 10 (1938).

The Shell Phosphate Process for the Removal of Hydrogen Sulfide

T. W. ROSEBAUGH
Shell Development Company
San Francisco, California

Presented at Eighth Mid-Year Meeting, American Petroleum Institute, Wichita, Kansas, May 24, 1938.

THE shell phosphate process is a regenerative liquid-purification system for the removal and recovery of hydrogen sulfide from natural or refinery gases and liquid hydrocarbons. The flow diagrams illustrate the four principal types of installations.

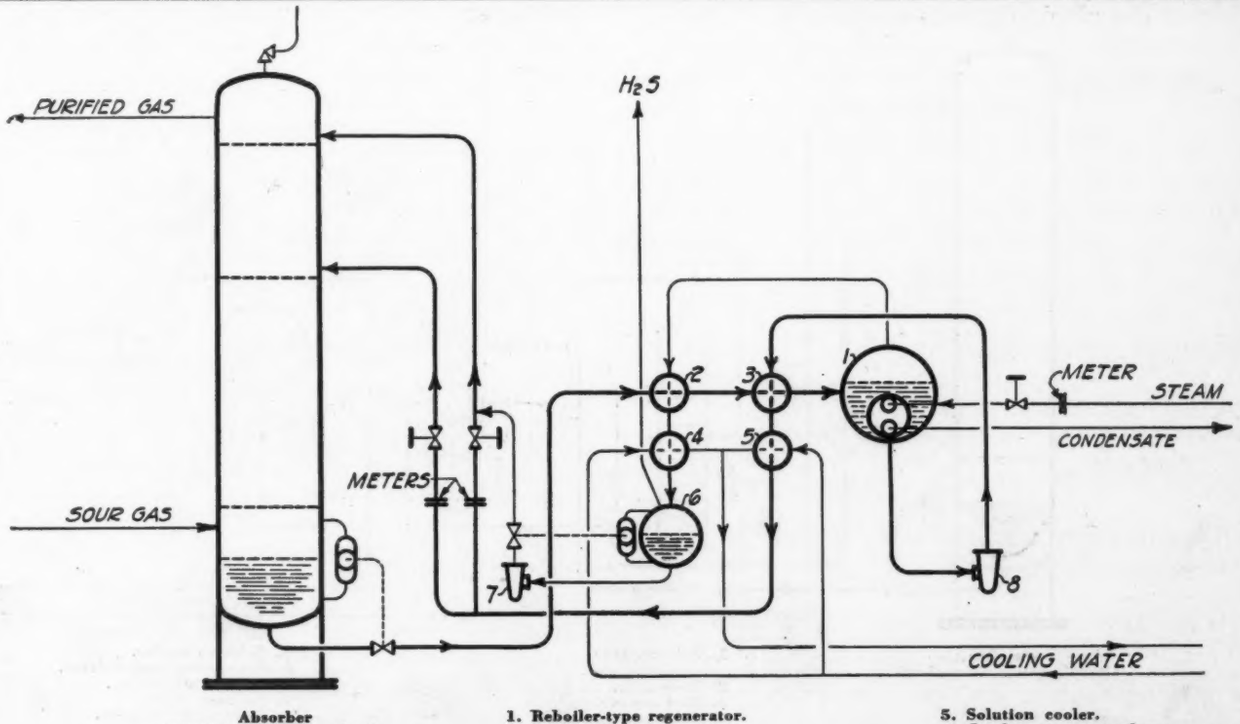
VAPOR-PHASE TREATING

The gas to be purified is scrubbed in a conventional bubble plate or packed absorber with an aqueous solution of tripotassium phosphate (K_3PO_4). Hydrogen sulfide is absorbed principally according to the reaction:

$$K_3PO_4 + H_2S = K_2HPO_4 + KHS$$

This reaction is reversed by boiling the solution. The vapor boiled off (hydrogen sulfide and steam) is condensed and cooled; the condensate is returned to the absorber, and the hydrogen sulfide is vented to suitable disposal; e.g., boiler fuel or to sulfuric-acid manufacture, sulfur recovery, process use, etc. The regeneration is usually accomplished in a standard reboiler heated with exhaust steam. In some cases a direct-fired regenerator may be used to advantage by employing a locomotive-type boiler for solution regeneration. High heat economy is realized through the use of exchangers on the solution to and from the regenerator. A final cooler lowers the temperature of the lean solution returned to the absorber.

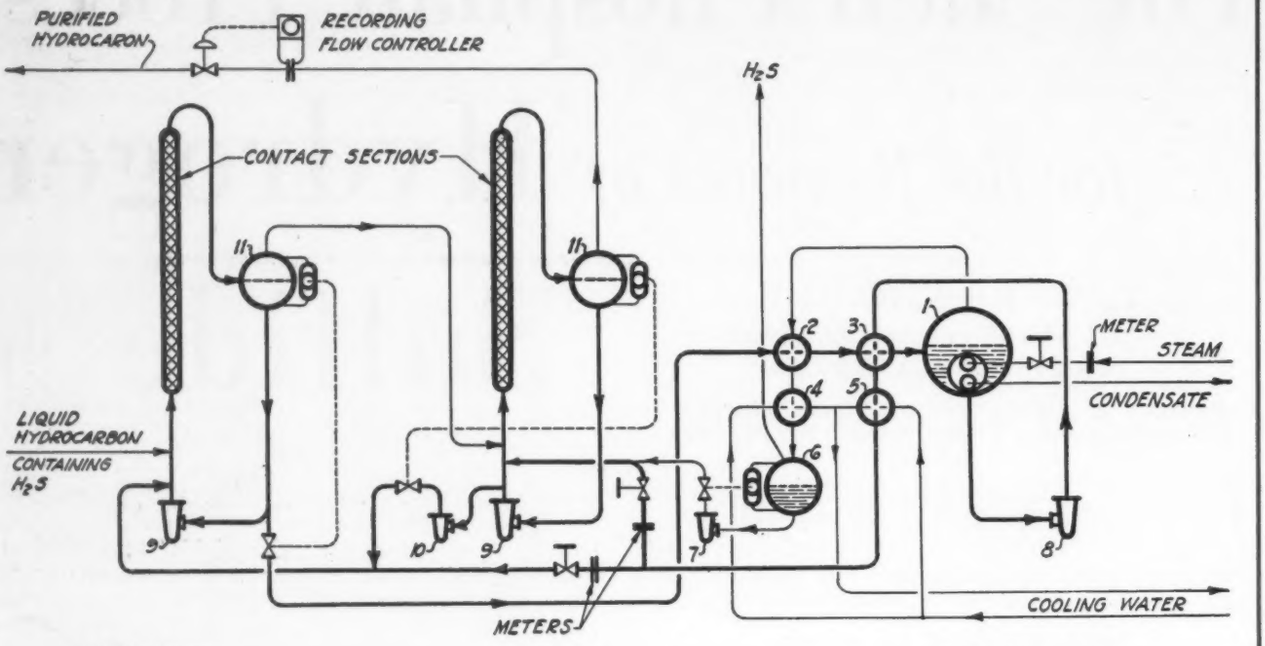
The solution used runs from 40 to 50 percent by weight of tripotassium phosphate. This inexpensive solution is prepared at the plant with commercial



Absorber
(Bubble plates or packed).

1. Reboiler-type regenerator.
2. Exchanger.
3. Exchanger.
4. Condenser.
5. Solution cooler.
6. Condensate accumulator.
7. Condensate pump.
8. Solution pump.

FIGURE 1
Shell Phosphate Process.
For removal of hydrogen sulfide from natural or refinery gases.

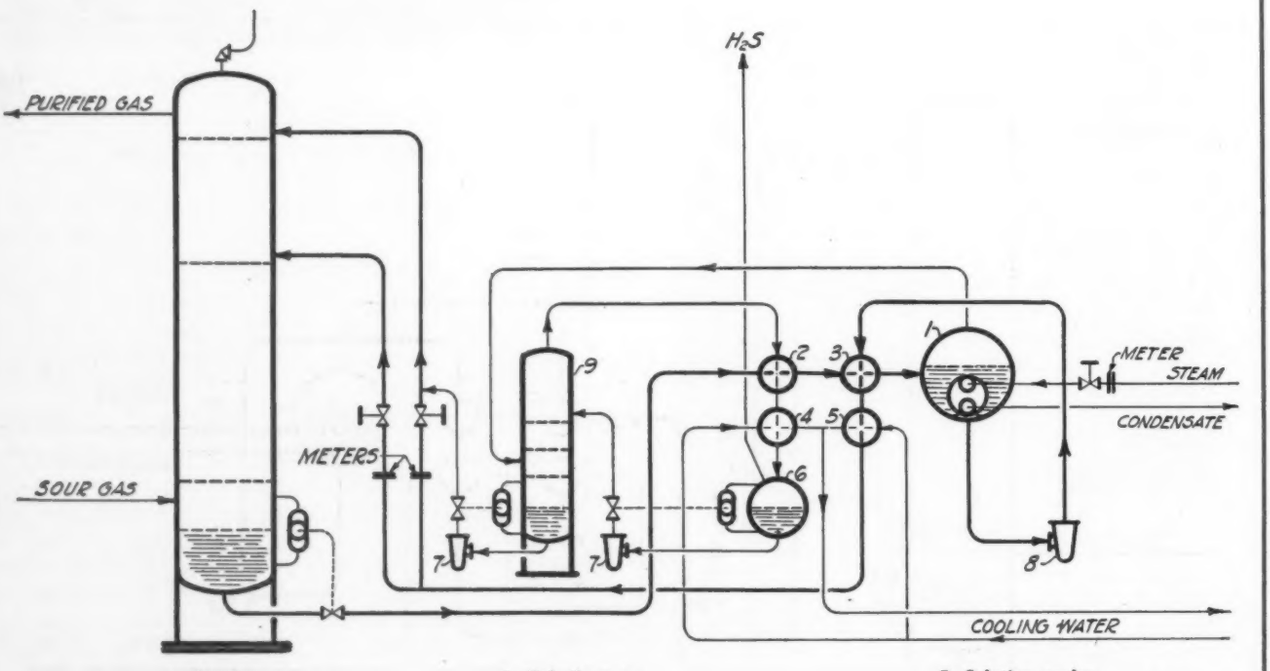


1. Reboiler-type regenerator.
2. Exchanger.
3. Exchanger.
4. Condenser.
5. Solution cooler.
6. Condensate accumulator.
7. Condensate pump.
8. Solution pump.
9. Circulating pumps.
10. Stage transfer pump.
11. Phase separators.

FIGURE 2

Shell Phosphate Process.

For removal of hydrogen sulfide from liquid hydrocarbons.



Absorber (Bubble plates or packed).

1. Reboiler-type regenerator.
2. Exchanger.
3. Exchanger.
4. Condenser.
5. Solution cooler.
6. Condensate accumulator.
7. Condensate pumps.
8. Solution pump.
9. Condensate stripper.

FIGURE 3

Shell Phosphate Process.

Hydrogen-sulfide removal for very high degree of purification (for liquid or vapor-phase treating).

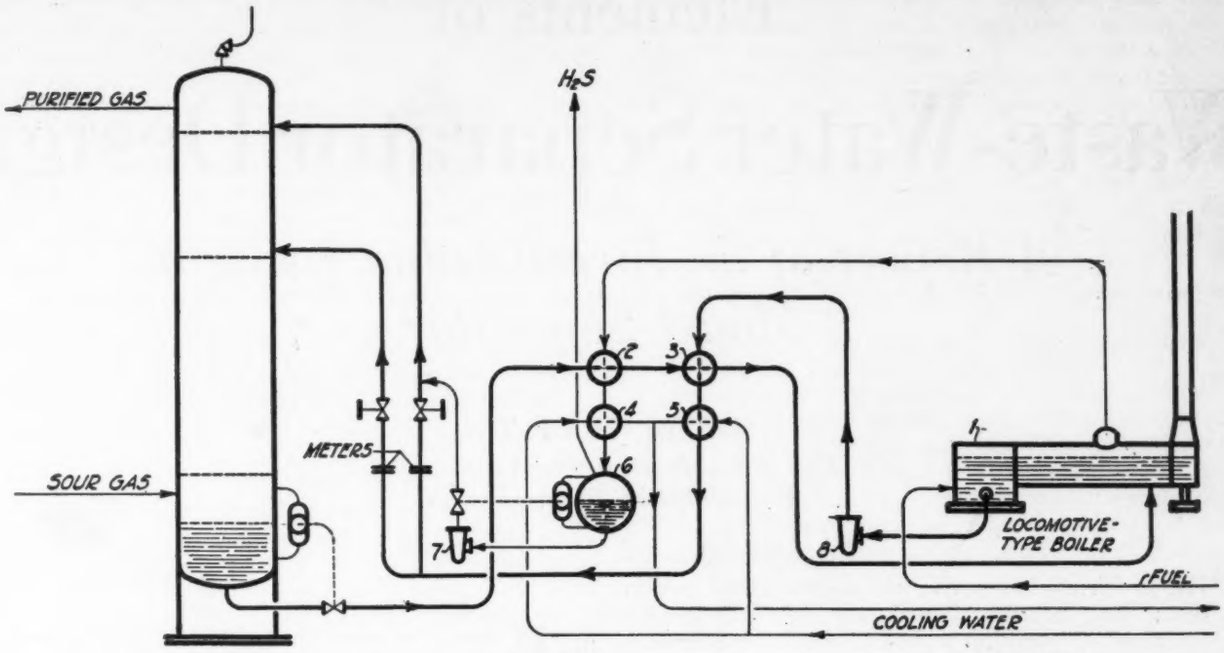


FIGURE 4

Shell Phosphate Process.

Hydrogen-sulfide removal using direct-fired regenerator (for liquid or vapor-phase treating).

grades of potassium hydroxide and of phosphoric acid. The initial charge lasts indefinitely, as solution loss is confined to packing-gland leakage on pumps.

The equilibrium vapor pressure of hydrogen sulfide over tripotassium-phosphate solution for a given hydrogen-sulfide saturation is greatly reduced upon diluting the solution with water. This reduction in vapor pressure with reduced tripotassium-phosphate concentration is peculiar to the phosphate process, and advantage is taken of this fact by using a system of split solution flow in the absorber. The bulk of the hydrogen sulfide is absorbed in the lower section of the absorber with a 40 to 50 percent solution, while the more difficult absorption at lower hydrogen-sulfide concentration is accomplished in the upper section with a relatively dilute solution.

The system of absorbing hydrogen sulfide with solutions of different concentrations makes it unnecessary to regenerate all of the solution to the lower degree of hydrogen-sulfide saturation required for a low hydrogen-sulfide content in the treated gas. The dilute solution is obtained by returning the condensate from the regenerator accumulator to the top of the absorber along with a small amount of the regenerated solution. The greater portion of the regenerated solution is returned to the lower section of the absorber.

The effect of solution strength on the hydrogen-sulfide vapor pressure for 20 and 50 percent tripotassium-phosphate solutions for comparison is illustrated by the equilibrium vapor-pressure curves of hydrogen sulfide over these solutions for various degrees of solution saturation.

For many installations the phosphate process may be used economically for treating gases at temperatures up to 200°F. This is often an advantage in purifying the gases supplied to polymerization plants.

LIQUID-PHASE TREATING

Liquid hydrocarbons may be treated for the removal of hydrogen sulfide. This is easily accomplished with the phosphate process, inasmuch as tripotassium-phosphate solutions are immiscible with hydrocarbons. Only one or two stages are necessary, depending upon the degree of purification required. The regeneration system is the same as that used for vapor-phase treating, and may be either the steam or direct-fired type. In liquid-phase as in vapor-phase treating, two-solution concentrations may be employed to advantage in a two-stage treatment.

ADVANTAGES OF THE PHOSPHATE PROCESS

1. The process is economical.
2. The process is practically non-corrosive to iron and steel equipment. (Copper or copper-bearing materials should not be used.)
3. Tripotassium phosphate is relatively inexpensive.
4. Loss of solution is confined to leakage, which may be controlled. There is no loss of treating agent to the gas or liquid being treated.
5. The process does not introduce catalyst poisons to the gas or liquid hydrocarbon treated for polymerization or other processing.
6. The process may be used economically for absorbing hydrogen sulfide at temperatures up to 200°F.
7. The process may be used for treating liquid hydrocarbons as well as gases, or a combination of treating steps using a common regenerating system may be employed.
8. Direct-fired regeneration may be used to ad-

[*Continued on page 288*]

Elements of
Waste-Water Separator Design
A Report of an Investigation Using a Model Separator

W. B. HART,
The Atlantic Refining Company,
Philadelphia, Pennsylvania

THE problem of removing oil from waste waters is one of long standing. In 1927 a survey to determine the extent of oil pollution was conducted by the American Petroleum Institute. In 1928, as a result of the survey, a Technical Committee for Prevention of Pollution was authorized and organized by the Institute. One of the first problems scheduled for investigation by this committee was separator design. Work on the solution of this problem was started in 1929.

When the Institute's Divisions of Production, Refining, and Marketing were organized, a waste-disposal committee was set up in each division. The problem of waste-water separator design became the major problem of the newly-formed Committee for the Disposal of Refinery Wastes. Many separators were studied in all sections of the country, with the thought that those found most effective would be carefully investigated and their desirable characteristics merged into a standard design for general application. This standard design became a part of Section I of the *Manual for Disposal of Refinery Wastes: "Waste Waters Containing Oil,"* published in 1931. There was ample justification for this procedure in the attitude of many states and the federal government in the matter of stream and tidal-water protection.

The separator design that evolved from the investigation just described was the result of a truly pioneering effort. In many respects it was very effective, but it had its limitations. Little criticism was heard for some time, however; for extremely few refineries made any attempt to apply the design. By about 1934 rumblings were heard from various localities. Many of the criticisms were the result of the increasingly drastic attitude of authorities in pollution prevention. Some were justifiable because of local conditions that were outside the limitations of the recommended design. Many were unjustified, and reflected a complete unfamiliarity with an increasingly important piece of petroleum-industry equipment.

The effect of these criticisms was the organizing of the country, by the committee, for a second study of separators. This study was carried out, and the results carefully examined. The group charged with the separator study on the East Coast was entirely convinced that no design reported possessed characteristics that would meet the really sound and constructive criticisms that had been directed at the standard design.

At a meeting of the East Coast group on July 10, 1936, the decision was reached that funds be requested for the building of an experimental separator for study of the problem. Approval of this procedure was given by the Executive Committee of the Institute on January 22, 1937, and the funds became available in July, 1937. The design of the separator was started immediately at the Philadelphia refinery of The Atlantic Refining Company. The model was constructed in the shops of the same plant, and was put into service at this plant in November, 1937.

IT should be stated that, although no large-sized separators have been constructed in accordance with the design data herein given, there is every reason to believe that they will discharge an effluent that will be satisfactory in any locality. It has been demonstrated that they will operate in accordance with the same natural laws as sedimentation chambers in sewage and water-purification practice. Investigators in these fields have shown that sedimentation phenomena may, in general, be successfully studied by the use of models, and the hydraulics duplicated in large prototypes. Duplication in separator effectiveness, should follow, therefore, inasmuch as it is dependent upon the same natural forces. Further, separator construction should not cause the tremendous expense that some anticipate. It is to be hoped separators will be constructed wherever necessary in order that the industry may rid itself of constant criticism, whether just or not, that the nation's waters are being polluted with oil.

This paper was presented at Eighth Mid-Year Meeting, American Petroleum Institute, Lassen Hotel, Wichita, Kansas, May 24, 1938.

FUNDAMENTALS OF OIL SEPARATORS

The first consideration in the design of a piece of equipment is to establish what the apparatus is to do. The second important item is to fix the limitations of application. This, in effect, means the determination of the extent of allowable operating costs that are reasonable in the light of a general idea of what the equipment is to do. If costs of construction and operation were not important, many methods of procedure would be open for the doing of a perfect piece of work; but this easy way is not possible. The third idea to be defined is the degree of efficiency to be set up as a goal

obtainable within the limits of reasonable application.

In the case of the waste-water separator, the purpose is to remove oil from waste water so the latter may be discharged to streams, etc., without creating oil pollution of these waters within the meaning of any rules or regulations that apply in the locality.

The limitations of reasonable operating costs define the limits to which it is reasonable to go in applying various engineering unit processes. These limits require that gravity be the main actuating force; that the simplest effective means for cleaning be employed; that the removal of the separated oil be accomplished with as little effort as possible, and a minimum amount of water be collected with the oil; that the ground space (plan area) be as small as possible; and, finally, that construction cost be as low as possible. Any reasonable unit-process application that aids in the above objectives is justified.

The third factor is the degree of perfection to be attained by the equipment. This may vary in different locations; but it can well be stated at this point that the probable best preventative for "regulationitis" is a sincere effort toward the greatest possible correction of the condition at which regulations might be aimed, particularly when this condition is palpably wrong. In the early stages of separator study, an allowable oil content of 30 p.p.m.* was established as satisfactory for effluents. This figure was based on the oil content in effluents from separators that seemed to be most effective at the time of the first survey. It was more or less arbitrary, and was determined by an analytical method that is open to a great deal of question—although it was the best known at the time. Since then, in many localities, this allowance is looked upon as much too high. Figures of the order of 5 p.p.m. are not uncommon requirements, and most existing and proposed laws state that no oil is permissible. In the design of the experimental separator used for fundamental study, the aim was to obtain an effluent that would be free of either iridescence or minute aggregates that would later liberate oil and cause iridescence.

Before discussing actual design fundamentals, another kind of limitation should be referred to. Specifically, this is the limit of the gravity-type separator which purports to separate oil from water when the oil exists in other than an absolutely free state. No gravity-type separator will separate oil from true emulsions, such as white water, where the oil is in the dispersed phase and the water in the continuous phase. Any emulsion of this type will pass through, and later create oil pollution in the stream receiving it, when the dilution is great enough to permit the oil to coalesce and break out as globules. This fact cannot be emphasized too strongly. It will be absolutely useless to construct a separator and expect its effluent to test free of oil unless provision is also made to correct this type of emulsion.

Certain so-called emulsions—loosely bound by a septum sustained by coke dust or fine clay—with oil in the continuous phase and water in the dispersed phase, will have a gravity that may be equal to, or greater or less than, water. Such masses will either sink or float; or, if in the aggregate they have the same gravity as water, they will move along with the water. They can be retained by a well-designed separator, and may be collected either from the surface of the water with the oil or from the bottom with the cleanings. This will be referred to in greater detail in the discussion of design.

* Parts per million.

Another limitation concerns the expectation that a separator operate by itself. Obviously, the equipment cannot be expected to function efficiently if it is filled with dirt, tar, silt, etc. Separators have been observed that would have operated in a reasonably efficient manner if cared for, but which had approximately 85 percent of their effective depth filled with solids. Others have been seen in which no oil had been taken off probably for months, and the water space was so filled with heavy oil that it was coming through the outlet. A separator constructed with the best intention will soon become ineffective if forgotten and left to operate and maintain itself.

Real progress in separator design began with the realization that the problem was closely allied to that of the sedimentation basin of the water-purification plant and the sludge-settling tank of the sewage-treatment plant. Prior to this time the problem was practically one of cut-and-try. Since this time, by taking advantage of principles developed by sanitary engineers and by modifying them to meet conditions involved, substantial advance has been effected.

The fundamental principles involved in the design of separators are substantially the following: Gravity-differential and water-gravity control; distribution; film destruction; and coalescence and filtration. These will be discussed in order. Other features will also be discussed as they are found to be part of main issues.

Gravity differential is the only actuating principle involved in separating oil and water, two immiscible substances. All other principles are employed to give gravity the maximum opportunity to operate.

If we were to place some water in a flask, float some oil on it, and somewhat violently agitate the whole mass of liquid, upon stopping the agitation and quickly examining the contents of the flask it would be seen that the oil had been broken up into globules, and that the globules had been distributed throughout the mass of water but were rapidly rising to the surface. It would also be seen that as each globule reached the surface it merged, or coalesced, with the oil film that had been formed almost as soon as the agitation had ceased. In this simple procedure is found all the elements of separator action. The agitation represents the action in the sewer, its junction boxes, etc.; when the agitation is stopped, there is the settling action of the separator. But this can only happen if the oil is free and not fixed in emulsions. Had an emulsifying agent been added to the flask, the agitation would have fixed much of the oil in emulsion form, and it would not have returned to the surface of the water. Rather, it would have been distributed throughout the water mass in minute globules, causing a milky turbidity. This happens readily in sewers or pumps if the right emulsifying agent is allowed to reach the sewer mixture of oil and water.

Much can be learned by considering the natural laws and examining the physical phenomena back of what has occurred in the flask. The first question, naturally: is what made the oil rise?

The answer to this question is that it was caused by the difference in specific gravity of the two substances. The specific gravity of water is 1.0; while that of the oil is either 1.0, or more or less than 1.0. To put it simply, if the oil has a specific gravity of less than 1.0, so it is, as we say, lighter than water, a globule of oil will be subjected to unbalanced gravitational forces resulting in its upward displacement, eventually to the top of the water. If the oil has a specific gravity greater than 1.0, i.e., is heavier than water, the resultant

displacement of an oil globule will be downward, until it reaches the bottom of the water. But if the oil has the same gravity as water, the globule neither rises nor falls, as the displacing pressure is the same above and below.

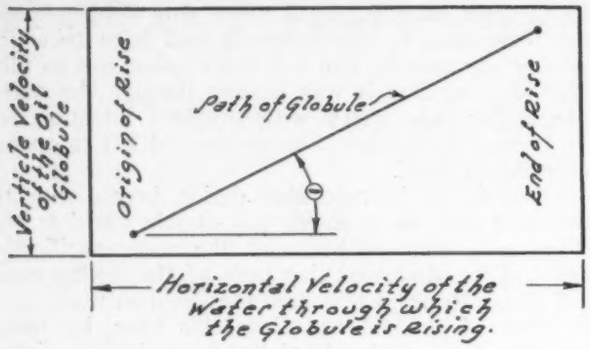

Vertical Velocity of the Oil Globule
Origin of Rise
Path of Globule
End of Rise
Horizontal Velocity of the Water through which the Globule is Rising.

FIGURE 1

The difference in gravity is also an important factor in the velocity with which the oil globule rises or falls. As mentioned previously, if the specific gravity of the oil is exactly 1.0, the globule will remain motionless—suspended in the quiescent water—because the latter has a specific gravity of 1.0; but, as the specific gravity of the oil becomes increasingly greater or less than 1.0, so will a globule of the oil sink or rise through the water with increasingly greater velocity. This is true only when the various globules are of the same diameter. The size of the globule influences its vertical velocity; the larger the diameter, the greater the velocity.

These facts play an important part in separator design, as is indicated in Figure 1. Study of this figure will show that it is the well-known force parallelogram in which the velocity of a globule of oil of a given diameter, and of a specific gravity less than 1.0, is related to the horizontal velocity of the water through which it is rising. The diagonal is the resultant path of the globule. Obviously, the greater the globule velocity, the greater will be the angle θ, and the shorter the required length of separator.

It would thus seem desirable to develop some mathematical method that would readily indicate vertical velocities or horizontal distances to allow for rise, so that all oil would be retained. This proposition was attacked from the basis of Stokes' law. The plan comprehended the calculation of sufficient factors to permit experimental check in an apparatus, such as shown in Figure 2. Considering first the basic law of Stokes, it may be expressed by the equation:

$$v = \frac{2}{9} gr^2 \left(\frac{s - s^1}{\mu} \right).$$

In which:

v = the velocity of subsidence, mm. per sec.
g = the acceleration of gravity, mm. per sec.
r = the radius of the particle, mm.
s = the specific gravity of the particle.
s^1 = the specific gravity of the liquid.
μ = the viscosity of the liquid.

With fixed specific gravity, the relation between the size of the particle, in millimeters, and the velocity of subsidence, in millimeters per second (hydraulic subsiding value) is not always a constant one. Hazen and others have shown that the velocity of subsidence for sand varies with the particle size as follows:

a. 1.00 m.m. and larger, as the square root of the diameter.
b. 0.10 mm. to 1.0 mm., as the diameter.
c. 0.10 and smaller, as the square of the diameter.

Thus, a particle of 1.0-mm. size will settle approximately 12 times as fast as one of 0.10-mm. size, and 650 times as fast as one of 0.01-mm. size.

The shape of the particle affects its subsidence rate because of skin effect.

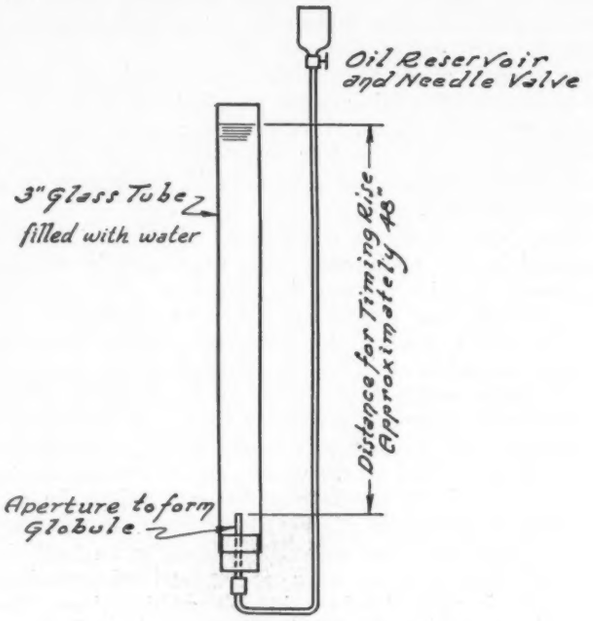

Oil Reservoir and Needle Valve
3" Glass Tube filled with water
Distance for Timing Rise Approximately 48"
Aperture to form Globule

FIGURE 2

Inasmuch as the volume and, as a result, the weight, varies as the cube of the diameter, and the surface area varies as the square of the diameter, it is evident that the surface area per unit of weight varies inversely as the diameter. Obviously, therefore, the smaller the size, the greater the surface area per unit of weight. For a given particle size, a spherical solid particle presents the least surface area per unit of weight. With angular, sharp-cornered, ovate, or other shaped particles the surface area and, as a result, the skin friction, will be greater (see Figure 3).

It should be noticed that, as the globule reduces in size, there is greater disagreement—probably indicating the influence of the higher-ratio zone of influence.

Before any mathematical design guide can be developed, other factors must be considered. Most important among these are: 1, temperature; and, 2, concentration of particles.

Temperature affects both the gravity and viscosity of the water through which the particle must travel. In order to clarify this effect, and to show the relationship between the effect on specific gravity and on viscosity, the experiments of Poiseuille offer an entering step. Based upon these experiments, the relation between the viscosity μ and the temperature T (° C.) is expressed:

$$\mu = \frac{0.0179}{1 + 0.03368\ T + 0.000221\ T^2}$$

The relation between the viscosity at any temperature t (° F.) to that at 50° F. is commonly taken as approximately:

$$\frac{60}{t + 10}$$

Hydraulic subsiding values of oil globules have been experimentally determined with the apparatus shown in Figure 2, and are compared with the findings of Hazen and others to the effect that solid particles of 1.0 mm. in diameter, or greater, vary in subsiding value as $\sqrt{a}$. The following experimental oil-particle velocities are corrected for water viscosity due to temperature:

For the oil particle $D =$

(a) 7.12 mm. hydraulic subsiding value 83.5 mm. per sec.
(b) 5.99 mm. hydraulic subsiding value 79.0 mm. per sec.

$$\therefore \sqrt{7.12} : \sqrt{5.99} : : 83.5 : 79.0$$
$$2.67 : 2.44 : : 83.5 : 79.0$$
$$2.67 \times 79.0 = 210.9 \qquad 2.44 \times 8.35 = 203.7$$

(c) 5.52 mm. hydraulic subsiding value 113 mm. per sec.
(d) 4.77 mm. hydraulic subsiding value 109.5 mm. per sec.

$$\therefore \sqrt{5.52} : \sqrt{4.77} : : 113.0 : 109.5$$
$$2.34 : 2.18 : : 113.0 : 109.5$$
$$2.34 \times 109.5 = 256.2 \qquad 2.18 \times 113.0 = 246.3$$

(e) 5.34 mm. hydraulic subsiding value 121.9 mm. per sec.
(f) 4.52 mm. hydraulic subsiding value 103.5 mm. per sec.

$$\therefore \sqrt{5.34} : \sqrt{4.52} : : 121.9 : 103.5$$
$$2.31 : 2.13 : : 121.9 : 103.5$$
$$2.31 \times 103.5 = 239.8 \qquad 2.13 \times 121.9 = 259.6$$

FIGURE 3

Hazen and others believed that, for particles smaller than 0.1 mm., viscosity controls the rate of settling; and that for particles larger than 1.0 mm., friction controls. In between the two sizes, both viscosity and friction were thought to be effective.

The relative effect of the two factors will depend on the size, shape, and specific gravity of the particles. It can be demonstrated, as shown by G. J. Schroepfer in *Sewage Works Journal*, **5** [2], an article from which much of the above data has been taken, that by substituting for

$$\mu \text{ the value } 0.013\frac{60}{t+10}(t \text{ in } ^\circ \text{F.}),$$

with v in mm. per sec. and d (diameter of particle) in mm., Stokes' law becomes:

$$v = 4.18\ (s - s^1)d^2\left(\frac{t+10}{60}\right)$$

Assuming sand with specific gravity of 2.65, and of uniform size of 0.1 mm., the formula becomes:

$$v = 4.18\ (2.65 - s^1)\left(\frac{t+10}{60}\right)$$

Assuming organic solids with a specific gravity of 1.20, and of uniform size equal to 0.1 mm., the formula becomes:

$$v = 4.18\ (1.20 - s^1)\left(\frac{t+10}{60}\right)$$

In the two equations above, $(2.65 - s^1)$ and $(1.20 - s^1)$, respectively, are the effect of gravity; and $\left(\frac{t+10}{60}\right)$ in each is the effect of viscosity. These are tabulated for various temperatures in Tables 1 and 2. Figure 4 gives the effects of temperature on specific gravity and viscosity of water. From Figure 4 it is evident that the changes in specific gravity of water, which are due to temperature, are too small to be of much importance. For the organic matter (specific gravity 1.20) the subsidence rate is increased only 2.5 percent by an increase in temperature of from 0 to 30° C. But for the same temperature range, the change in viscosity brings about an increase in subsidence velocity of 129 percent. This is much more important than the increase from the specific-gravity change. The major importance of specific gravity is its influence in causing currents and stratification, thereby reducing actual detention time.

TABLE 1

Effect of Specific Gravity and Viscosity on Subsidence for Particles of 0.1 Mm.

(Specific gravity, 2.65)

Temperature (° C.)	$(2.65 - s^1)$	$\left(\frac{t+10}{60}\right)$	Product	v Equals:
0	1.6505	0.70	1.158	4.85
10	1.6505	1.00	1.650	6.90
20	1.6520	1.30	2.150	9.00
30	1.6550	1.60	2.650	11.10
Increase from 0 to 30 per cent	100.3	228.5	228.8	228.8

TABLE 2

Effect of Specific Gravity and Viscosity on Subsidence for Particles of 0.1 Mm.

(Specific gravity, 1.20)

Temperature (° C.)	$(1.20 - s^1)$	$\left(\frac{t+10}{60}\right)$	Product	v Equals:
0	0.2005	0.70	0.140	0.586
10	0.2005	1.00	0.200	0.837
20	0.2020	1.80	0.262	1.100
30	0.2050	1.60	0.328	1.370
Increase from 0 to 30, per cent	100.2	228.5	234.3	233.8

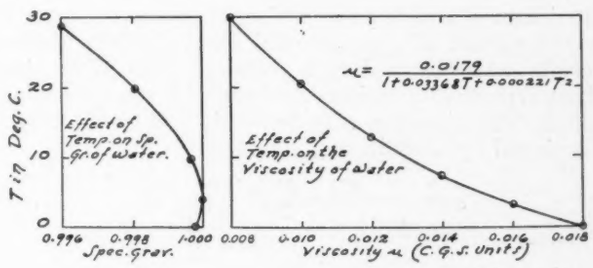


FIGURE 4

The effect of concentration or density of particles in a fluid is believed to be one of joining together of smaller particles into larger ones of increased subsidence rate. This may come about either because of cohesion or flocculation.

All the above factors are discussed from the standpoint of solid particles that are heavier than water. It is reasonable to believe, and experiment has confirmed to a reasonable degree, that they may be applied to globules of liquid that are immiscible with water and that are lighter or heavier than water. Mathematically, the relation becomes one of a negative or positive sign in solving the equation for Stokes' law.

When consideration of the problem is focused directly upon globules of oil as the suspended particles, but with water still as the mass in which they are suspended, certain other factors present themselves. They

result from the mobility of the oil, which causes the particle continually to change its shape. The temperature, by reducing the viscosity of the water, adds to the ease with which the shape of the globule is changed; also, by causing expansion, it results in a change in the specific gravity of the globule.

The globule of oil in traveling through the water meets resistance to the line of travel, and tends to flatten at the poles of this axis. The result is easier motion in a side direction, until resistance again changes its course. The path of travel, therefore, becomes a zigzag one—which not only decreases considerably the net subsidence velocity by creating a longer path, but also adds to the resistance due to skin friction.

Of greater importance is the change in specific gravity. Oil expands rather rapidly when heated, while water expands to a much lesser degree. Assume that a globule of oil weighing 1.05 g. has a volume of 1 ml. Such a globule would displace 1 g. of water, and would sink because it displaces less than its own weight. Now assume that there has been an equal and considerable increase in temperature in the oil and water. The water expands but little while the oil changes in volume from 1 ml. to 1.1 ml. The globule now displaces 1.1 ml. of water which weighs 1.1 g., while its own weight is still but 1.05 g. The globule will now rise, because it displaces less than its own weight.

When all the foregoing data were examined, formulated into a usable tool, and applied to problems that would permit of experimental check, a coincidence in results was obtained that followed reasonably closely those reported by various workers with sewage sedimentation. These results may be condensed to the formula developed by Babbitt and Schlenz:

$$R = \frac{(D + 226)C}{3.72\left(C + \frac{216 - D}{4}\right)}$$

In which:
R = the percentage removal.
D = detention period, min.
C = concentration of oil, p.p.m. inlet.
Solving for *D*, the equation becomes:

$$D = \frac{[3.72R(C + 54)] - 226C}{C + 0.93R}$$

Assuming a normal sewer delivery of about 10,000 p.p.m. of oil, and assuming a requirement of 100 percent removal, the best estimate that can be made of detention time with any procedure we have at hand today is that determined by the above formula. Solving the equation, the required detention time would be 348 minutes, or 5.8 hours. This would mean that, for every 1,000,000 gallons of waste water there would be required 241,700 gallons of sedimentation capacity in the form of a separator of the order of 50 feet wide, 110 feet long, and 6 feet deep. Every factor that will contribute a reduction of this equipment size is of value. Among these factors, all of which are accessory—inasmuch as their purpose is to provide optimum conditions for gravity differential to operate—are distribution, film rupture, scrubbing, or absorption, combined with coalescence, and filtration.

Distribution may be defined as the delivery of flow to the sedimentation chamber in equal rate to every cross-section point, so that each vertical cross-sectional plane follows the other in orderly fashion. Under such conditions, a globule of oil will rise or sink in the same manner as through quiescent water, except that it will be influenced by the horizontal velocity of the moving water. This is the condition of Figure 1.

Emphasis has been placed on the necessity for the oil being free—not bound in emulsions of high stability. There have also been mentioned so-called emulsions which are not highly stabilized. As a rule, in these the oil is in the continuous phase and water is in the dispersed phase. Usually the mass of emulsion is bound by a film or membrane in the form of a "glob" or "liver," as it is sometimes called. By the rupture of this film, and of internal films, the glob may be progressively broken down into particles of oil, each subject to the conditions of its own gravity.

Other conditions to which this fundamental is important is the case of the particle of silt upon the surface of which is held a layer of oil assumed to be of a thickness of one molecule. Gas bubbles from putrescent water or bottom settlings will also become carriers of oil. Conversely, a particle of oil may be the nucleus carrying a layer of silt or coke. In any such case the gravity of the aggregate may be the same as the water, and the oil in the mass will not be retained. Further, by freeing the oil either from the loose emulsion or from the oil-silt, gas-oil, or oil-coke aggregates, the free oil will have opportunity to join other particles to form larger globules of higher hydraulic sedimentation rate. When the process of film rupture and coalescence is conducted right in a mass of oil, there is a real absorption by the oil mass; and, to a large extent, incoming oil is scrubbed out of the water and retained.

It has been found that by far the greatest part of the retention time is required for the removal of the last few parts per million of oil. Any procedure or device that can be substituted for sedimentation will greatly reduce the size of the separator and, therefore, its costs. Such a procedure is filtration. This is a well-known unit process of chemical engineering, and needs no further explanation—other than to say that, to some degree, its effectiveness is due to absorption by the cloth used. More or less frequent flushing of the cloth is necessary, as the layer of suspended matter builds up and retards the passage of the water.

APPLICATION OF THE FUNDAMENTALS

Knowledge of fundamentals is of little value without the additional knowledge of how to use them. The first question in this connection is how to control the gravity of the water from which the oil is to be separated, and then how to provide for the optimum functioning of gravity differential.

Control of the waste-water gravity is a matter of controlling the wastes discharged to the sewers which deliver to the separator. High acidity, i.e., that will lower the pH* of the water below about 4.5, should be prevented. Likewise, high alkalinity, i.e., that raises the pH above about 10.0, will cause difficulty in many instances. High dissolved solids may also affect gravity, and should not exceed 1000 p.p.m. Inasmuch as these conditions are matters of water pollution themselves, their correction serves a double purpose. For the same reason, their control is a distinct feature in itself, and is not detailed here.

The most important condition for bringing about optimum functioning of gravity differential is good distribution. What is meant by distribution has been outlined. How to obtain it is sometimes difficult, as is also protection of the distribution after it is obtained. In general, it may be said that distribution is obtained by

* Hydrogen-ion concentration.

dissipation of the kinetic energy in the flow of water as it enters the separator. Although this sounds simple, many devices and combinations of devices have failed to obtain better than 60- to 70-percent efficiency. Methods that have been applied vary greatly; but, in

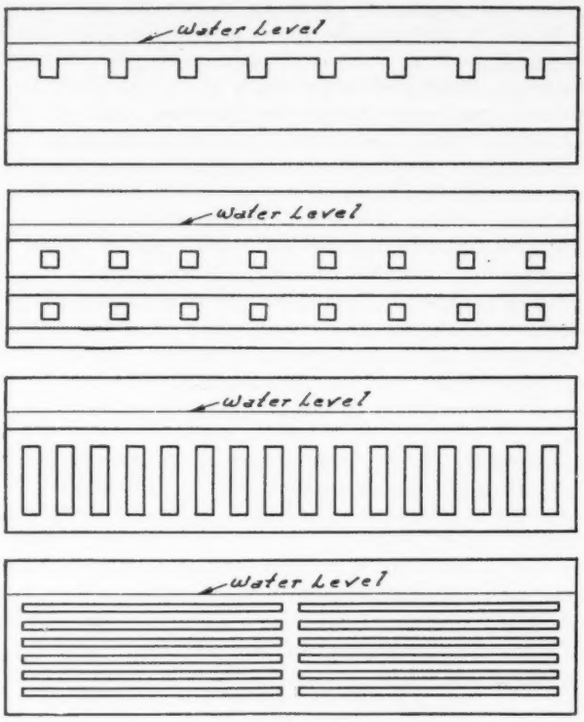


FIGURE 5

general, they consist of baffling the high-velocity flow as it leaves the sewer pipe—spreading this flow laterally, and then introducing the fluid into the settling basin over weirs, through ported baffles, through stone-filled boxes that cause sufficient head loss to distribute the flow, or through slotted baffles in which the slots run either vertically or horizontally. More highly developed slotted baffles are equipped with shutters by which the flow through the slots can be controlled individually or by groups. Various types of distribution weirs and baffles are shown in Figure 5.

The installation of a weir or baffle in a sedimentation chamber does not mean that the greatest possible distribution is assured. Regardless of the extensive studies and experiments that have been made, it is still recommended by those best versed in the subject that baffling be held to a minimum. And of particular importance is the recommendation that no baffle be firmly fixed in place. Instead, it should be movable both vertically and horizontally, and in operation should be located by trial with the actual chamber in which it is to be used. Also, experience has shown that most effective application points for weirs or baffles are at the inlet and outlet zones, leaving an undisturbed space in the main body of the chamber for gravity differential to exert full play.

Much study and effort may be exerted to obtain the best possible distribution; and then, through some seemingly unimportant feature of design, the efficiency will be destroyed. In this connection, one of the common design errors is to place angular supports or other structure in the main body of the separator. Any columns, supports, or other structural features in the water body should be designed in "streamline" cross-section in the direction of flow, with ample radii wherever necessary. The careful attention that is due the item of distribution because of its importance is worthless and wasted unless the precautions to protect the distribution are also employed.

For the rupture of films or membranes, heat, agitation, or actual puncture is effective. These processes may all be carried out in the presence of a large mass of oil, thereby promoting coalescence and the formation of large globules of high hydraulic sedimentation rate.

Filtration is a matter of mechanical application and operation that permits flushing of the cloth. The rate of flow also is important. Best results are obtained at a rate which does not exceed 0.5 cubic feet per square foot per minute.

The application of these fundamentals will be most apparent from their application in the experimental separator.

THE EXPERIMENTAL SEPARATOR

In the development of a design for the experimental separator, consideration was given the following fundamentals:

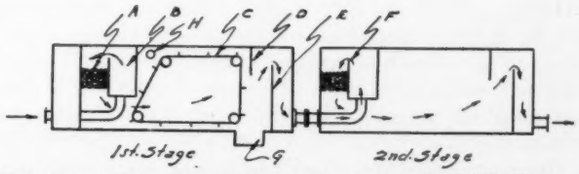
From the standpoint of construction—

a. Gravity differential.
b. Film rupture and coalescence.
c. Globule size.
d. Distribution.
e. Retention time.
f. Depth of flow.
g. Ratio of width to length.
h. Baffling.
i. Oil clean-up vs. water clean-up.
j. Iridescence retention.
k. Aeration and oxygen absorption.

From the standpoint of operation—

a. Removal of settled material.
b. Removal of separated oil.
c. Control of water gravity.
d. Control of water viscosity.
e. Control of oil gravity.
f. Measurement of flow.

It would be of no particular value to detail here the extensive calculations, design sketches, paper work, etc., that attended the preparation of plans for the separator. Rather, suffice it to say that a fixed width was set that would permit the equipment to be handled on a freight car. All other dimensions were made variable in greater or lesser degree.



A—The stone cell for film-rupture coalescence and distribution.
B—The inlet distribution chamber for dissipating energy of inlet flow.
C—The flight-scraper cleaning device.
D—The oil-retention baffle.
E—The out-fall weir.
F—The inlet distribution weir—same in both stages.
G—Slurry-collecting chamber.
H—Oil-skimming slotted pipe.

FIGURE 6

The Experimental Separator in Section.

The various fundamentals are worthy of brief discussion concerning their application, as shown in Figure 6.

Gravity differential has been described as being the only basic fundamental of the procedure. It needs no further discussion here.

Film rupture and coalescence were provided for in the stone-filled cell shown in Figure 6. By placing this as shown, the entire flow of the separator is passed through the cell, in which is retained a mass of oil, so that film rupture and coalescence may occur

as much as possible. It is important that the flow pass through the cell from top to bottom, inasmuch as the stone- or clinker-fill acts both as a filter and distributor. Should stoppage occur, the distribution provided by the weir which precedes the cell will be interferred with by channel effects. The flow from top to bottom will bring any such stoppage at the top of the cell, where the stone or cinder may readily be stirred up and cleared.

Globule size is also provided for by the cell. To the degree that every particle of oil is caused to coalesce and that the accumulated oil fills the stone cell, eventually the oil will reach the water bottom of the cell and pass on into the sedimentation section. In doing so, with no confining orifice or other restraint, only large globules of oil will detach themselves. These will have a high hydraulic sedimentation rate, and will come to the surface in a very short length of separator.

The question of a choice between weirs and baffles for distribution required considerable study. Weirs alone, baffles alone, and a combination of the two were considered. Knowing the controversial aspect of any discussion of weirs vs. baffles, and also knowing the critical effect of baffle position, the final decision was to use inlet and outlet weirs as distributors, with no baffling of any kind in the sedimentation space except a short oil retainer at the outlet end. This type of design has proved its value. Under closely-controlled conditions of operation and material to be handled, baffles would possibly give a greater efficiency; but, for general application, where simplicity and a minimum of attention are factors, the weir is the most satisfactory, over-all efficient device.

Fixing a definite retention time was a troublesome question. Calculated retention requirements were immediately seen to be out of any reasonable range, and there was no real guide to a definite figure. It was a fortunate circumstance that final filtration was studied at this same time. This procedure held out promise of such good results that finally retention time was left open, it being planned that varying retention periods would be tried and results noted.

Depth of flow, as well as the relation between width and length, is debatable. Some will argue that by using great depth a longer retention period can be obtained with less ground space. Others will argue that shallow separators will result in a shorter path for a particle either to rise or to sink and be retained. In the final analysis, it will be found that both depth and width influence distribution to a great extent. Too much depth will permit gravity and temperature to operate, and produce stratification and short-circuiting. Too little depth will tend to reduce retention time, but probably will aid distribution. As a result, there is an approximate balance within a certain zone. By this is meant that there is probably little to choose between, say, 6 feet and 8 feet as depth figures; but between 6 feet and, say, 16 feet the shallow separator is more desirable.

A shallow separator is more likely to be uniform in action, and is easier to keep clean. Its construction cost will also be less in many cases. The depth of the experimental separator was set at an average of 3 feet, so that any working equipment calculated from the model would have a depth that would not be unreasonable or interfere with distribution efficiency.

A somewhat more definite idea of width and length may be had from other factors. For example, the separator must be long enough to permit the oil globules to come to the surface so they may be retained. This length must include the necessary factor of safety. As to the width, it is more or less governed by the requirements of weir length to give proper distribution without too great a head loss. No logical relationship that can be mathematically expressed has been found. Without such a logical basis or, in fact, any real evidence of an optimum ratio of width to length, it is a matter of common sense to give the separator the most efficient length, and then make it wide enough to bring about the necessary head loss over the weir to give good distribution. Such a ratio may vary anywhere from the width equal to one half the length to the width equal to the length.

It will be noted that no mention has been made of velocity of flow, a matter that was continually stressed in the first separator-design recommendation. The only consideration given velocity in our present knowledge of separator design is that the separator should not be made so narrow, in relation to its length, that a high velocity is developed in the flow—a high velocity in this case meaning something in excess of 3 feet to 4 feet per minute. A separator which in each stage or section is from one third to one half as wide as it is long seems most logical, and also lends itself well to unit construction.

Baffling, unless of intricate design that would permit extensive variation in application, would probably cause more difficulty than it would return in value. In attempting to increase distribution efficiency, or simplify oil collection, it is very easy to bring about an exactly opposite effect. If intricate baffles are used, it is next to impossible to translate their design and position in the model into terms of application to large-size equipment. Hence, no baffles are used in the model separator other than the small oil retainer at the outlet end—which was previously referred to—and the out-fall baffle, which in reality is an outlet-end distribution weir.

Oil clean-up vs. water clean-up is probably a phase that will puzzle many. It is used for want of a better one that is a brief. What it refers to is that one set of conditions is efficient and practical for removing most of the oil. An entirely different set of conditions is necessary for the final clean-up of the water before disposal. In retaining and collecting the major portion of the oil, there will be a corresponding retention of the major portion of the settleable solids. Provision must be made for the removal of this material. In collecting the oil it must be brought to the collecting system in some manner and picked up. While the disturbance caused by the frequency of these operations may be of little moment in the first case, it might be sufficient to upset the very necessary quiescence in the water-clean-up phase. In the latter case, it might be said at this time that an attempt was made to use the law of surface attraction for water clean-up by suspending wooden slats in the flow. The principle involved is that the minute particles of oil or other suspended matter could accumulate on these surfaces and be retained. This procedure returned no increase in clean-up, and it is believed the eddy currents resulting from the obstacles and corners probably carried the particles away from the surfaces, so that cohesion had little chance to operate. The final development was a two-stage separator in

which the separate functionings were provided for in separate compartments.

The removal of all iridescence seemed to be a hopeless problem when sedimentation alone was employed. True, by reducing the flow so that the retention period approximated the calculated figure, iridescence was minimized to a degree that could be called practical elimination. Yet every so often a particle would come along that had so nearly the same gravity as the water that it was carried out with the effluent. When it was further agitated, the oil would break out and produce the rainbow effect so well known. The removal of these particles seemed possible only by filtration. When this was tried, its effectivenes through such a large range of flow rates was so favorable that it was immediately recognized as being the answer to reduction in retention time and separator size. Its use was at once provided for, but not in the actual separator design. The simplified application was developed after the experimental separator was in use; therefore, the design features will be a separate matter.

To many, aeration and oxygen absorption will mean little; but it is a matter that must be given consideration in many sections of the country. Refinery waste waters frequently carry odors of naphtha that are not difficult to remove by agitation. This is not true of waste-water odors resulting from disposal of waste caustics and similar substances. These should never reach the sewer without first having been subjected to odor-removal processing. Dissolved oxygen in varying degree is also a requirement in some localities. To provide for this, the experimental separator was constructed with an out-fall weir that splashed the water around as it cascaded down from the crest. In this manner much of the odor will be released, and at times as much as 1.5 to 2.5 p.p.m. of oxygen is absorbed.

Turning now to fundamentals of operation, the first and foremost involves keeping the separator clean so that its ability to function is maintained at all times. This was one of the main complaints received concerning the original design in Section I of the Institute's manual. Even though it is hard to understand how a sedimentation chamber, no matter how inefficient, can be expected to keep itself from filling up, an attempt was made to provide a means for easily keeping the equipment clean—both at the bottom and at the surface. The best method found takes the form of what is known as a "flight scraper." It consists of a continuous pair of chains, motor-driven, which carry cross-planks at even intervals. The planks travel along the surface of the water, about one half of the lower part being below the surface so that the layer of oil is moved forward into a slotted pipe which is placed across the entrance end of the sedimentation section. This pipe may be rotated so that the lower edge of the slot can be adjusted accurately to skim all the oil with very little water. One bearing on which the slotted pipe rotated is a lead-off line to a tank in which the skimmed oil is collected to be pumped away. As the planks or flights move on around, they pass under the surface, downward, and then along the bottom where they move the settled material to a bottom recess from which it may be cleaned out in slurry form to a draining tank or board, either under hydrostatic head or by pumping. The water drains off and returns to the separator; the solids are then disposed of in the most advantageous manner. The flight scraper is only operated as needed, perhaps two or three times in 24 hours. It creates practically no disturbance, for its forward velocity is only 1 foot per minute. Right here it should be stated that this combination of equipment is a plain "steal" from the sewage-disposal procedures.

The control of water gravity is not exactly an essential feature, but a highly desirable one. High acidity, high alkalinity, and excessive dissolved solids —all will change the gravity so that disturbance will result in the separator. Inasmuch as these conditions are in themselves problems of proper waste disposal, and have been mentioned previously, no further consideration is given the matter here.

Control of water viscosity is a fundamental that has been amply discussed. The warmer the water, the better the separation. To warm the water on purpose would be a costly procedure as a rule, but every effort should be made to conserve any heat that the waste may carry. This statement must be qualified in the event the heat of the discharge waste water may seriously affect the temperature of the body of water receiving it.

The control of oil gravity is another matter that will be necessary in only rare instances, i. e., when

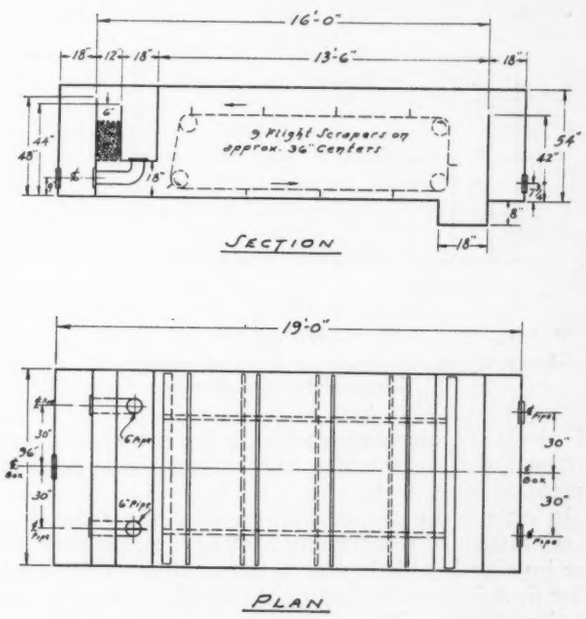


FIGURE 7
A Sketch of the First, or Oil-Recovery, Stage—Major Dimensions Are Shown.

the waste to be sepaarted has a gravity very close to that of water. Under these circumstances, a lighter oil may readily be sprayed into the stone chamber or cell to mix with the waste, and produce an average gravity that will have a satisfactory hydraulic sedimentation rate. Laboratory investigation should be resorted to in order to determine the most satisfactory oil to use for mixing.

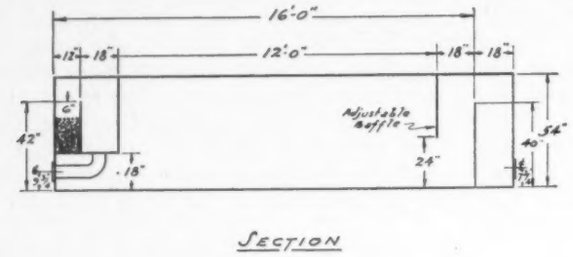
The rate of flow through any separator is valuable information. Water-pumping costs have been reduced by the operator of the separator when he has been able to see that an excessive flow was coming through. Frequently the reduction comes about by eliminating unnecessary flow to condensers or idle equipment. In some localities, it is required that the rate of flow be reported.

For the experimental separator, a special weir box was provided. In the plant equipment, the out-fall

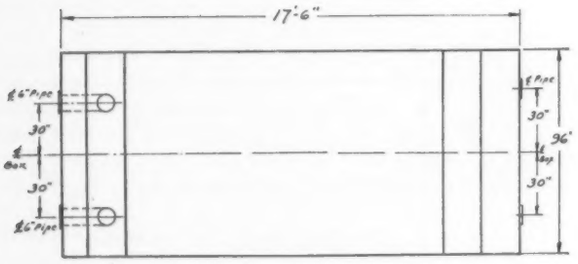
weir may be used as a measuring device to obtain a very close approximation of the flow.

DIMENSIONAL DATA FOR THE SEPARATOR

Figures 7 and 8 illustrate better than pages of explanation just how the experimental separator was constructed. Interest will center on the dimensions, the results obtained, and a method for translating these results into dimensions for plant-size equipment. Again referring to Figure 6, the dimensional relation to the assembly is made clear. The only further detail necessary was that the equipment be an all-steel, welded job so designed as to give an average



SECTION



PLAN

FIGURE 8

A Sketch of the Second, or Water-Clean-Up Stage—Major Dimensions Are Shown.

of about 25 percent variation in practically every dimension except width, which was fixed for transportation at 8 feet.

In examining the effectiveness of the separator, it is necessary to understand that two separate features are involved. This is due to the testing methods used. The first feature is that of the total ether extractable in the effluent. The second is the visible iridescence on the effluent.

In making comparisons on the basis of the first test, it should be understood that the test consists of flocculation of all suspended matter in the effluent sample, filtering off the floc, and extracting it for 2 hours with refluxed ether. The ether is then evaporated from a measuring tube of special design, and the organic matter remaining measured by volume. The sample taken approximates one quart; and, after it has been emptied from the bottle, the latter is washed with ether, which is then filtered and added to that in the extraction.

It will be realized at once that this is a most drastic test. It recovers all organic matter present. Since Schuylkill River water, which is heavily laden with domestic sewage, is the plant water supply, there are reported by the test all the colloidal sewage fats, oil, and other organic matter. It is not surprising, therefore, that this test gives results of from 5 to 25 p.p.m. of ether extractable. River water has been shown to have the same range. In fact, there are tests of record to show an organic content of 37 p.p.m.

TABLE 3

Operating Conditions

WATER USED	Rate (Cu. Ft. Per Min.)	Retention Period (Minutes)		Calculated Forward Velocity (Ft. per Min.)
		Calculated	At 55-Percent Efficiency	
1. Waste water from cracking area, tank bottoms, stabilization and polymerization plants	8	112	56	0.38
	12	74	37	0.43
	16	56	28	0.57
	36	26	13	1.28
2. Waste water from drawing down tank bottoms*	24	36	18	0.86
	40	23	11	1.43

Examination of Effluent

TEST No.	Rate (Cu. Ft. per Min.)	pH†	Ether Extractable (P.P.M.‡)	Turbidity (P.P.M.‡)
1	8	6.9	17	100
1	12	7.0	21	77
1	16	6.8	22	58
1	36	6.9	25	72
2	24	..	20	..
2	40	..	28	..

* This test run at Sun Oil Co. refinery, Marcus Hook, Pa.
† Hydrogen-ion concentration.
‡ Parts per million.

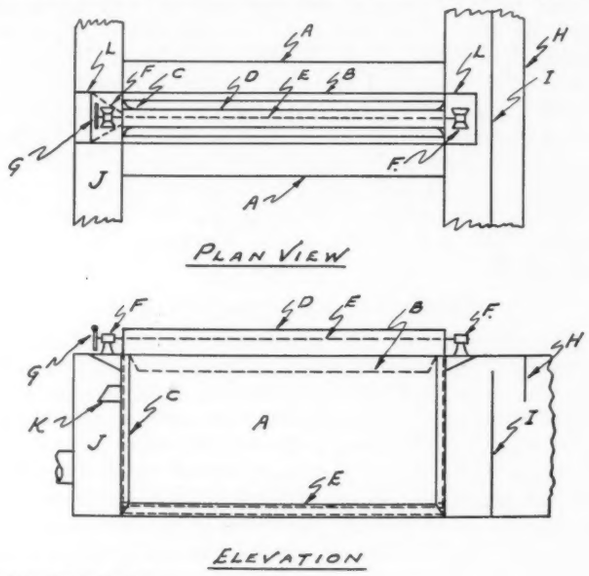
The visual test for fluorescence is a much more valuable one by which to gauge the effectiveness. This is particularly true when there is also information as to turbidity of the effluent. The latter will show the presence or absence of emulsions. A turbidity test of 25 p.p.m., as shown by the Jackson turbidimeter, will indicate a clarity in which emulsions and colloids are at a minimum. When suspended matter is also known, a complete story is available.

Based upon these understandings, the average effectiveness as shown in Table 3 was obtained.

At first glance it would seem that these results are not very favorable. With full understanding of what they indicate, they tell a considerable story. They are all taken from tests in which sedimentation alone was used. They were made using wastes of about the meanest characteristics that will be encountered. Of greatest interest is the wide range of capacity with little change in effluent; the fact that no filter was used; that from the turbidity there was an unsuspected amount of both emulsion and colloidal matter in the water which markedly increases the ether extractable, and that the iridescence on the effluent and small "rainbow-producing" particles were at a minimum. The indicated next procedure was the removal of these visible conditions by filtration. Inasmuch as cooperation with certain authorities required that the equipment be moved to another refinery at this time, the experimental work on filtration was continued at Philadelphia as a separate investigation.

With the realization that sewage fats, etc., were always possibilities, the work was based on removing iridescence and suspended particles that would produce iridescence when released. Crude screens applied to existing plant separators had already demonstrated that this could be done, even though the filtering agent was only cheesecloth. Examination and experiment was started with various types of cotton and wool cloths to determine their filter rate

and their ability to retain the iridescence. The experiments conducted show that, even with a rather tightly-woven cloth, a filtering rate that is not prohibitive is possible. The most important information obtained, however, was that the rate to be used in practice was not governed by what could be put through the filter, but by how slowly it must be put through the cloth to retain the iridescence. It was also learned that careful consideration must be given this rate so as to retain an almost balanced head on both sides of the filter, or serious mechanical difficulties will be encountered. On several occasions seemingly contradictory results were obtained. These were discouraging until their cause was discovered. First ideas were that only the upper layers of the flow need be filtered. This was soon found to be quite incorrect; for particles passed under the screen, and iridescence on the effluent resulted. Again, when a



A—The filter tank.
B—Distributing baffle.
C—Rubber seals sustained by spring clips.
D—Revolving filter or screen.
E—Shafts.
F—Bearings.
G—Worm-and-gear drive.
H—Oil-retaining baffle of separator.
I—Out-fall distributing weir of separator.
J—Outlet compartment of filter.
K—Outlet from filter proper.
L—Platforms.

FIGURE 9
General Filter Construction.

full-sized screen was built and put into service, some oil film came through. The cloth used was one that in the laboratory had shown much promise. But when the screen was taken out of service and examined, it was found that every fiber was in such tension that practically open holes existed. Investigation revealed that, when the screen had been made, the cloth had been carefully stretched and fastened to the frame. Inasmuch as there is always some shrinkage, when the screen was put in service the cloth was pulled so tight that it could do no filtering. When filters are constructed, there must be allowance for this.

Calculations for applying a filter to the experimental separator indicated that a cross-sectional filter would not provide the necessary area to permit the required filtering rate. It was necessary, therefore, to design a unit that could be used in multiples of a required size to give the necessary area. The matter was discussed with continuous-screen manufacturers, and a very practical and usable unit designed. It may be installed independently, and as much area provided as needed without very much additional space. The filter is of the continuous-rotating type in a separate tank which is arranged to distribute the flow equally to all parts of the filtering area. Figure 9 shows the general construction clearly. One or more units of the required size may be installed as an addition to the separator, parallel to the long axis, and ample filter area provided.

The filter is made up of a sufficiently stiff wire as a support, and over this the filter cloth is placed—making ample allowance for shrinkage. This is one case where a rather rumpled cloth will do a better job than a smooth neat one, for the neat one will probably be pulled open. There is a considerable choice of cloth to use. Strangely enough, a horse blanket is extremely good, but has a very low rate. A fairly tight weave is best, but it should not be too close. Flannel is very effective. Present the rough side to the incoming flow. No matter what cloth is used, a spray system of 25 to 30 pounds pressure should play on the cloth to flush it off continuously. The washings are caught in a trough and returned to the separator.

TRANSFERENCE FROM MODEL TO PLANT DESIGN

To facilitate the application of experience with a model to prototypes of a size for plant use, it is necessary to develop transference equations. The transfer must be made in accordance with the principles of similitude, so that the large-size equipment will have the same hydraulic characteristics as the model. This is not entirely possible, because water under the same gravitational force is used in both the model and the prototype; but the deviation is negligible.

It is believed that a definite advance would result from the designing of a standard separator unit. This can be done as an example of the application of the transference equations, and thereby a double purpose will be served. The first question involves the quantity of waste water to set up as the capacity of the standard unit. Refinery-water consumption ranges from practically none, in plants where water is scarce and re-circulation is employed, to figures of the order of 100,000,000 gallons per day. It is believed that a figure of 5,000,000 gallons per day would have the most general application.

It is also necessary to choose a capacity for the model upon which to base transfer equations. Several factors must be considered in this choice; for the capacity of a separator should not be set at the normal process load only. In many cases, storm run-off water and fire stream run-off must be included. Such a condition requires that the separator be effective over a wide range. The model separator exhibited such a range of from 4 to 40 cubic feet per minute. With this condition in mind, and to insure effectiveness at all times, the capacity chosen for the model is 25 cubic feet per minute. With the capacity set for the model and its prototype, we may proceed with the transference equations. Several phases of similarity are involved—mainly geometrical, kinematical, and dynamical. These will be discussed in turn.

Making use of the capacities chosen, we have that for the model 25 cubic feet per minute and for the prototype [(5,000,000 gallons $\div$ 7.5 (gallons per cubic foot) $\div$ 1,440 (minutes per day)] = 463 cubic feet per minute. At first glance it would seem that the transference factor would be $463 + 25 = 18.32$, and

that all dimensions would be multiplied by this factor. Should this be done, it would be found that the developed separator would be unnecessarily large and entirely different in hydraulic values from the model.

However, by applying the formulas of dimensional analysis as set forth by Marzolo, Reynolds, Chick, and others, it is necessary first to find a "scale of length ratio" upon which all relations are based. In the case of the separator, the efficiency is to a large extent dependent upon retention. Retention is a function of cubic content of the sedimentation section. Designating linear dimensions by L, areas by A, volumes by V, and the scale of length ratio by λ, and identifying those dimensions of the model by the subscript m:

$$L = \lambda L_m$$
$$A = \lambda^2 A_m$$
$$V = \lambda^3{}_m$$

Selecting the volume equation $V = \lambda^3 V_m$ and substituting the volumes per minute chosen for prototype and model:

$$463 = \lambda^3\, 25$$
$$\lambda^3 = 463 \div 25 = 18.32$$
$$\lambda = 2.65$$

The "scale of length ratio," therefore, is 2.65; and the length L, the width W, and the depth D of the standard unit may be found by:

$$L_m \times 2.65 = 16 \times 2.65 = 42 \text{ ft. } 6 \text{ in.}$$
$$W_m \times 2.65 = 8 \times 2.65 = 21 \text{ ft. } 3 \text{ in.}$$
$$D_m \times 2.65 = 3.5 \times 2.65 = 9 \text{ ft. } 3 \text{ in.}$$

The sedimentation section in both the first and second stages, therefore, will be 42 feet 6 inches long, 21 feet 3 inches wide, and 9 feet 3 inches deep.

For complete hydraulic similarity, the velocity must also be considered. This factor, as previously mentioned, cannot be perfectly transferred, inasmuch as gravitational effects are involved. Within very close limits, the calculated velocity of the model may be transferred by the formula:

$$v = \sqrt{\lambda v_m}$$

The calculated velocity of the model, assuming 100-percent distribution, is 0.893 feet per minute:

$$v = \sqrt{2.65} \times 0.893 = 1.45 \text{ ft. per min.}$$

In this way the factors of capacity, dimensions, retention period, and velocity are fixed. It now becomes necessary to provide the distribution to protect the hydraulic characteristics they contribute. This is a matter of weirs and head loss, and involves an entirely different analysis. The head on the crest of the weir box must be sufficient to assure a flow that is as nearly equal as it is possible to make it at all points of its length. Inasmuch as the quantity of water is the same over the out-fall weir as on the inlet weir, the head on the former can be used to avoid possible interference by the stone-cell action with the latter. Applying Francis' formula for weirs:

$$Q = \tfrac{2}{3}(0.622 h b \sqrt{2gh})\text{; and solving for } h$$

$$h = \sqrt{\frac{2.25Q^2}{0.387b^2 2g}}$$

In which:

h = head on the weir, ft.
Q = flow over the weir, cu. ft. per sec.
b = breadth of the weir.
g = 32.16 (use 32).

In the case of the model, $Q = 0.41$ and $b = 8$.

Therefore:

$$h = \sqrt[3]{\frac{2.25 \times 0.41^2}{0.387 \times 64 \times 64}} = 0.062 \text{ ft.} = 0.75 \text{ in.}$$

In the case of the standard, $Q = 7.7$ and $b = 21.25$
Therefore:

$$h = \sqrt[3]{\frac{2.25 \times 7.7^2}{0.387 \times 451.5 \times 64}} = 0.22 \text{ ft.} = 2.6 \text{ in.}$$

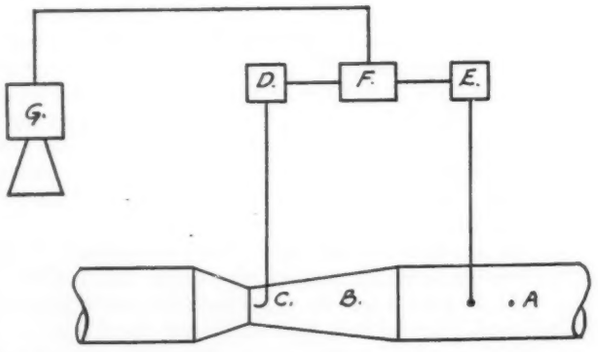
With this head on the weir, there will be ample flow to assure a good distribution.

Returning again to the dimensional similarity factor of 2.65, the dimensions of the weir box, the stone chamber and all other linear factors may be worked out with the assurance that the hydraulics will not be changed in any great degree.

In delivering to the weir box, it should be remembered that, whereas only two 6-inch lines were used in the model, in the standard, smaller lines will be used, and more of them will add much to the distribution efficiency. This part of the design is individual to itself, and should be looked at from the standpoint that there are 463 cubic feet per minute, or 7.7 cubic feet per second, to be carried into the box. The velocity in the lines should be as low as it can be made conveniently. For the standard, ten 10-inch lines evenly distributed would give a satisfactory velocity. They should be branches of a header into which the sewer discharge is centrally connected.

CONSTRUCTION MATERIALS

Examination of the reports covering the various separator surveys revealed that in nearly every instance concrete was used for construction. In many instances this is unnecessary. Welded-steel construction will prove satisfactory, even though the waste water is acid; for this condition can be corrected before the waste water reaches the separator. Acid waste is a pollutant even though no oil be present, and should be neutralized. By doing so, costly form work for concrete construction can be avoided, and long life can be obtained from ordinary tank steel. The correction procedure is one of pH control by the dry or wet feeding of a neutralizing agent, the most economical probably being soda ash. Inasmuch as both rate of flow and variation in acidity are involved, two sets of controls are necessary. They interact to modify each other. The make-up of this equipment is understandable from Figure 10. By its use a range of control within one point of pH value is



A—Point to be controlled.
B—Venturi tube.
C—Head tube of Venturi meter.
D—Flow meter for rate of flow impulse.
E—pH meter for acidity impulse.
F—Modifier which averages the two impulses to control the chemical feeder.
G—Chemical feeder and mixing devices.

FIGURE 10
Electrically-Operated pH Control.

readily possible, and this is ample for both metal protection and acid-pollution prevention. The equipment is of very recent design, and would probably have to be calibrated and adjusted in the field.

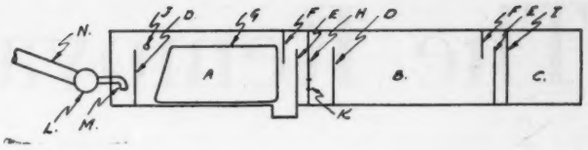
SEPARATORS FOR LIGHT AND HEAVY OILS

When a plant is so organized that light oils are handled separately from the heavier products, it is possible to effect an economy in construction. Separators for retaining slop oils above a gravity of about 42° A.P.I. will not, as a rule, be called upon to handle "globs" of loosely-bound so-called emulsions. The oils that come to them will usually be quite free, and will separate readily. Such separators should be constructed without the stone cell or weir box. An entrance weir, with the flow introduced well below its crest, from a manifold and through as many connections as can be made conveniently, will give very satisfactory results. The "flight-scraper" device should be installed in the first stage to keep the sedimentation chamber clean, and ample filtering should follow the second stage. The sedimentation section should not deviate from the standard.

Separators for handling waste waters from areas where heavy oils of any nature are processed or stored should be constructed in accordance with the general design features of the model so that every fundamental is included. It should be realized that blindly following the model design in every detail is not necessary nor desirable. For example, there is no occasion for the separation of the two stages as in the model, nor for the flanged and bracket construction which make possible the variation of dimensions. Figure 11 shows the construction of a separator for use with light oils, and also shows a method for combining the first and second stages in any separator.

CONCLUSION

It should be stated that, although no large-sized separators have been constructed in accordance with the design data herein given, there is every reason to believe that they will discharge an effluent that will be satisfactory in any locality. It has been demonstrated that they will operate in accordance with the same natural laws as sedimentation chambers in sewage and water-purification practice. Investigators in these fields have shown that sedimentation phenomena may, in general, be successfully studied by the use of models, and the hydraulics duplicated in large prototypes. Duplication in separator effectiveness should follow, therefore, inasmuch as it is dependent upon the same natural forces. Further, separator construction should not cause the



A—First stage.
B—Second stage.
C—Filter-tank section.
D—Inlet-end distribution weir.
E—Outlet-end distribution weir.
F—Oil-retainer baffles.
G—Flight scraper.
H—Dividing wall between first and second stage.
I—Dividing wall between second stage and filter.
J—Oil collector—slotted pipe adjustable by rotation.
K—Inlet ports to second stage—pipes are used with a weir box.
L—Distribution manifold ahead of separator.
M—Inlet pipes with turned-down ells.
N—Sewer.

Showing method of combining first and second stages—which differs from model. For heavy-oil separator, other features of model are included, but stages are combined as above.

FIGURE 11
Basic Design of Light-Oil Separator.

tremendous expense that some anticipate. It is to be hoped separators will be constructed wherever necessary in order that the industry may rid itself of constant criticism, whether just or not, that the nation's waters are being polluted with oil.

ACKNOWLEDGMENT

In preparing this paper, particularly those parts dealing with sedimentation chambers, filtration, cleaning devices, etc., information and assistance have been had from many sources. Among those who generously gave of their time and knowledge, the author's thanks are extended to: L. V. Carpenter, professor at New York University; and to the following gentlemen: S. E. Kappe, of the Chicago Pump Company; W. R. Marshall and Mr. Quinn, of the Chain Belt Company; H. R. Schwarz, of Wellington Sears Company; J. M. Hines and D. C. Converse, of Builders Iron Foundry; and L. R. Whitcomb, of the Syntron Philadelphia Company.

BIBLIOGRAPHY

[1] G. J. Schroepfer, "Factors Affecting the Efficiency of Sewage Sedimentation," *Sewage Works J.* **5**, 209 (1933).
[2] L. V. Carpenter and H. W. Speiden, "Notes on Sedimentation," *Sewage Works J.* 7 [2] 200 (1935).
[3] C. H. Capen, Jr., "Study of Sewage Settling-Tank Design," *Eng. News-Digest* Nov. 24 (1927).
[4] "Motion of Solid Particles in Liquid," *J. Inst. Mining Eng. (London)* **77**, 65 (1928).
[5] H. E. Babbitt and H. E. Schlenz, "Results of Tests of Sewage Treatment," *Illinois Eng. Exp. Sta. Bull. 198* (1929).
[6] Allen Hazen, "On Sedimentation," *Trans. Am. Soc. Civil Eng.* **53**, 45 (1904).
[7] Arthur B. Morrill, "Sedimentation Basin Research and Design," *J. Am. Water Works Assn.* **24**, 1443 (1932).
[8] *Hydraulic Laboratory Practice*, American Society of Mechanical Engineers (1929).

The Removal of Inorganic Salts from Crude Petroleum

DE-SALTING systems in use in a number of Mid-Continent refineries are described.

Two satisfactory continuous methods for salt removal have been developed in the laboratory. One process involves repeated washing of oil through a sodium-carbonate solution at 200° F. during 20 minutes and subsequent settling at this temperature. A continuous addition of less than 3 percent of 0.3 percent sodium-carbonate solution is required.

The second and preferable method involves emulsification of 3 percent of 0.3 percent sodium-carbonate solution, percolation of the mixture through an excelsior column at 250° F. during 20 minutes, and settling at 250° F. for 50 minutes. A removal of 80 percent of the salt is accomplished.

Comparison of laboratory data with plant results indicates that the success in laboratory experiments could be approximately duplicated on a commercial scale.

A column packed with excelsior is more effective in resolving and emulsion than a corresponding mineral bed.

This paper was presented at Eighth Mid-Year Meeting, American Petroleum Institute, Wichita, Kansas, May 24, 1938.

WENDELL P. HAWTHORNE
and
H. L. BEDELL
Socony Vacuum Oil Co., Inc.
White Eagle Division, Augusta, Kansas.

CRUDE petroleum, as received in the refinery, almost invariably contains inorganic salts. Occasionally these salts are present as solid particles which are associated with wax crystals or surrounded by amorphous wax.[1, 2, 37] Usually, however, the salts are present in an aqueous solution which is emulsified with the crude oil.

Deposits of petroleum are commonly found associated with an aqueous salt solution. It is questionable whether this salt solution ever passes through an oil-bearing sand in the form of an emulsion with the petroleum; for filtration through a sand layer has a decided tendency to break such an emulsion.[1] Rather, it seems probable that oil and water enter the well hole separately, and suspension of one phase in the other follows.

After once entering this chamber, the oil and water have innumerable opportunities for emulsification. Whenever the mixture is subjected to a rapid motion or to a shearing force, there is a tendency for one liquid to become dispersed in the form of small drops in the other. The extent to which this emulsification takes place is dependent, to a large degree, on the quality of the equipment used and upon its state of repair.[1, 3]

The mechanical treatment which the oil-water mixture receives determines not only the amount of water emulsified, but also the state of subdivision of the dispersed phase and, therefore, the difficulty to be encountered in resolving the emulsion. A portion of the internal phase is usually dispersed in such large particles that it is comparatively readily removed by settling. Another part, however, may be dispersed as a true colloid or emulsoid; i. e., the particles may be so small that electrical effects and Brownian movement will prevent any settling.[1]

Before petroleum is transported in pipe lines, the water content is reduced to a comparatively low figure. At the time of this removal of water, a large part of the associated salt is also removed, and the salt content of pipe-line crude oil usually does not exceed about 150 pounds per 1000 barrels (expressed as NaCl) although the amount is quite variable.[2, 4] (150 pounds per 1000 barrels is equivalent to 25 grains per gallon or 68.1 grams per barrel.) This first reduction of salt content is accomplished by means which will be mentioned briefly in a later part of this paper. The reduction is probably achieved through removal of the larger particles of the dispersed phase.

For the formation of a stable emulsion from two liquids, the two must be nearly immiscible. In general, some substance termed an emulsifying agent must be present. When the two liquids are agitated together, the surface tensions of the two tend to dictate which liquid will assume the dispersed form. The suspended particles acquire like electric charges, and these charges tend to stabilize the dispersion. In the presence of a third substance, an emulsifying agent, a more stable emulsion results. Such an emulsifying agent is usually a protective colloid, and is preferentially wetted by one phase or the other. If preferentially wetted by the oil phase, the colloid is termed hydrophobic, and an emulsion is formed in which water is the internal phase. This type of emulsion is found almost invariably when crude petroleum and water become mixed.[1, 3, 5, 6, 7]

Dow's investigations of crude-oil emulsions indicate that asphalt is present as a hydrophobic colloid, and that this colloid stabilizes the water-in-oil dispersion. The increased concentration of asphalt at oil-water interfaces has been demonstrated by analyses of oil separated from an emulsion and of asso-

ciated comparatively-dry oil. Asphaltic material has been separated from oil, and has been found to be effective as an agent for emulsifying water in kerosene. Finally, a study of different types of oils showed that a naphthene-base petroleum easily gave stable emulsions with water, while no emulsions could be formed with a paraffin-base oil.[1, 7]

Petroleum emulsions are found to become increasingly stable with age. This change is thought to be due to a slow adsorption of colloidally-dispersed material at the oil-water interfaces. For this reason emulsions are preferably treated for resolution as soon as possible after formation.[3, 8]

The extensive acid treatment of wells has, presumably, considerably increased the difficulties which may be traced to the salt in crude oil. This treatment has tended to increase the concentration of chlorides of calcium and magnesium for insoluble calcium, and magnesium salts are converted to the soluble chlorides.

The salts to be found in crude oil are, of course, variable. Often sodium chloride is predominant, while appreciable amounts of calcium and magnesium chlorides are present.[2, 9, 11] Egloff and co-workers have reported analyses of the salt contents of crude oils from a large number of fields.[37]

OBJECTS OF SALT REMOVAL

The removal of inorganic salts from crude petroleum may be attempted for any of a number of reasons. The reasons effective in one refinery differ from those applicable in another, as the operation of the plant varies or as the products vary.

When chlorides of calcium or magnesium enter distillation equipment associated with crude oil and water, the conditions prevailing are such that these salts hydrolyze to yield free hydrogen chloride. This, in solution, is a very destructive corrosive agent. The acid is especially active in attacking condenser sections; for the conditions are suitable for solution of the hydrogen chloride in liquid water. Often the cost for replacing condenser tubes and the time required for their replacement become important items. Ammonia is regularly used to combat this type of corrosion in many refineries, and serves to combine with the hydrogen chloride. Although ammonia prevents the corrosive action of the hydrogen chloride, difficulty may be experienced through deposition of solid ammonium chloride in condenser tubes in such amounts that these tubes become clogged. At times the deposition takes place inside of a fractionating column, and interferes with satisfactory operation.[2, 4, 9, 10, 11, 12]

In a number of refineries the prime object in introducing de-salting units has been the prevention of the formation of salt deposits. "In general, salt in the crude in any appreciable amount deposits in the heat exchangers or the first few tubes in the still, leading to local hot spots, tube blistering, and clogging—sometimes to the point of necessitating cleaning the tubes by steam, water, or mechanical devices."[10]

If cracking equipment is supplied with residual oil, this charging stock contains salts originally present in the crude oil. It has been proved that these salts have an extensive effect toward inducing coke formation during cracking. The formation of such coke deposits often limits the time during which a cracking unit may be kept in continuous operation. Coke deposits may contain as much as 50 percent of salt.[2, 9, 11]

Corrosion due to salt is also encountered in cracking units which operate upon residual oil. Hanson[9] estimates that corrosion will be noticeable in cracking operation if combined calcium and magnesium chlorides exceed 25 pounds per 1000 barrels of charging stock (11.4 grams per barrel).

An important incentive to salt removal for those refiners who prepare "straight-run asphalt" is the increase in the solubility of such asphalt in carbon tetrachloride and carbon disulfide made possible by salt removal. In many refineries it is impossible to meet the state specifications without some system of salt removal.[2, 9] In addition fuel oils, produced either by cracking or primary reduction, may fail to meet numerous specifications, such as the Navy's, unless provision is made for salt removal.

W. P. HAWTHORNE

Wendell P. Hawthorne was granted the degree B.S. by Tarkio College, Tarkio, Missouri, in 1929, and Ph.D. by Cornell University in 1933, where he majored in physical chemistry. For the past four years he has been research chemist for the White Eagle Division of Socony-Vacuum Oil Company, with headquarters at Augusta, Kansas.

H. L. BEDELL

H. L. Bedell was graduated with the degree B.S. in 1921 and M.S. in 1924, by the University of Nebraska, and for the next two years engaged in public school work. Currently he is chemist for White Eagle Division of Socony-Vacuum Oil Company, with headquarters at Augusta, Kansas.

METHODS FOR TREATING OIL-FIELD EMULSIONS

In treating a crude petroleum to reduce the salt content, the general method is to reduce the water content; i. e., salt present is usually closely associated with water, and a reduction in water content brings a parallel reduction in salt content.

Pipe-line crude oil is fairly low in water and sediment. Inasmuch as it is generally easier to reduce the water percentage from 3 percent to 0.6 percent

than from 0.3 percent to 0.06 percent, the common methods of de-salting involve emulsification of some added water—the amount may vary widely with the method. This water is mixed sufficiently intimately that salts are more or less uniformly distributed through the added liquid. Finally, the emulsion is broken by some means to yield a crude of low water and sediment and of low salt content.

Thus, in essence, de-salting methods are really only methods for breaking a water-in-oil emulsion, and methods applicable for breaking an oil-field emulsion to yield pipe-line crude oil are generally applicable for breaking an intentionally-prepared emulsion to give a low salt content. For this reason general methods which have been used for breaking oil-field emulsions will be briefly reviewed.

Simple settling is the earliest of these methods. The separation depends upon a low viscosity and a large difference between the specific gravities of the two phases. The method is slow and inefficient. A layer of viscous emulsion usually results. Exposure of the emulsion to sunlight and percolation through a layer of separated brine have both been found to improve the simple settling process.[1, 8, 13]

At elevated temperatures settling proceeds more rapidly. The rise in temperature results in a decreased viscosity, in an increased difference in specific gravity and, possibly, in a solution of colloidal emulsifying agents. Washing of emulsion through a layer of hot brine is again found to give improved coalescence of water droplets.[1, 5, 6, 8, 13]

Centrifugal treatment offers a means of magnifying greatly the difference in specific gravity between oil and water. The separating force applied to an emulsion in a good centrifuge may be thousands of times as great as that produced by gravity alone, and a comparatively rapid separation of water occurs. It is to be pointed out, however, that while the centrifuge greatly increases the rate of settling of water, it has but little effect on the rate of coalescence. The tendency, then, is to yield dry oil and a water-in-oil emulsion which is very rich in water rather than a distinct water phase.

Commercial applications of both Sharples and De-Laval machines have been made. Heating, re-centrifuging, and the addition of chemicals have all been used to advantage. The presence of dirt or solid matter in the oil introduces complications.[1, 8, 13]

As a further addition to this list of more or less mechanical means of separating emulsions, we may mention filtration or treatment by contact with a solid agent. When an emulsion is treated with such a material, it is not planned that water shall be removed. Rather, the contact with the solid causes coalescence of water particles to form particles of such a size that these drops can subsequently be removed by settling. In such a treatment the solid agent is preferentially wetted by the internal phase of the emulsion—by water in the case of oil-field emulsions. Sand, excelsior, clay, diatomaceous earth, and other solids have been used commercially in this way. In addition, the use of a number of solids such as steel wool, crystallized alumina, hematite, lepidolite, hornblende, cloth, etc., for this purpose has been patented. Such solid agents are usually employed in conjunction with other methods of treatment.[1, 5, 8, 13, 14]

The two methods which have been used most extensively for separating oil-field emulsions are chemical treatment and electrical dehydration. Each is used with some system of settling.

Dow[1] has divided chemical treating agents into six groups. Some compounds actually combine with water present. Some cause flocculation of hydrophobic protective colloids. Sodium carbonate is a member of a group that reacts with salts in the water phase or with acids in the oil phase.[13] Members of a fourth group produce oil-in-water emulsions, and so tend to invert crude-oil emulsions. This group is most widely employed, and includes sodium soaps, resins and resin soaps, gums, starch, sulfonates of organic acids, etc. Tretolite compounds are usually in this class.[1, 3, 6, 8, 13] The two remaining groups include electrolytes, which cause adsorption of positive ions on negatively-charged water droplets, and organic solvents which dissolve the protective film about dispersed particles.

In a typical application of Tretolite the reagent is added to the emulsion in a flow line; and the mixture is heated, sprayed upward through a layer of brine, and settled while hot.[1, 3, 13, 14]

Mention is made in the literature of the application of many compounds as chemical treating agents. Patents refer to the use of alkali sludge,[15, 16] sulfonates, acid sludge, neutralized acid sludge, etc. Many soaps have been recommended.[17, 18, 19, 20] Sodium hydroxide, sulfuric acid, and phenol are repeatedly mentioned. Naphthenic acids have been recommended and used as demulsifying agents.[21, 22] A number of petroleum products have been suggested. Cracked residues, oil-oxidation products,[23, 24, 25] and the extracted oil from the Edeleanu process[26] are all said to aid resolution.

Electrical dehydration is accomplished by passage of the emulsion through an electric field. Both alternating and direct-current systems have been employed, but the use of an alternating current is most common. In this case particles are not attracted to either electrode, but the stresses produced result in coalescence of small particles to drops which settle readily. The system is applied to a preheated emulsion, and an appreciable time is allowed for settling. Potential differences of 33,000 volts between the electrodes are usual.[1, 8, 13, 14]

METHODS IN USE FOR THE REDUCTION OF THE SALT CONTENT OF CRUDE PETROLEUM

The literature pertaining to the treatment of pipe-line crude oil for reduction of salt content is all comparatively recent, and but a small number of articles have been published.

As previously mentioned, the methods which have been proposed or used for reducing the salt content of pipe-line crude oil are essentially the same as those formerly applied to the breaking of oil-field emulsions. Simple settling of the pipe-line crude oil at elevated temperatures has been tried; but, in general, very unsatisfactory removal is secured when a practical time of settling is employed. Simple settling after emulsification of added water has, however, been applied with some improvement.

In 1934 C. R. Wagner[27] patented a process in which oil is emulsified with a quantity of water (up to 5 percent) by a closely-controlled method, and the resulting emulsion is allowed to separate by settling. A refinery installed in Alma, Michigan, in the spring of 1936[12] uses this general system. At first, settling without the addition of water was attempted. Oil was preheated to 250°F. and settled at this tem-

perature, and at a pressure of 50 to 60 pounds per square inch. Some salt removal was observed. However, addition of 10 to 12 percent of water at the crude-charging pump resulted in greatly improved operation. A reduction of salt content from 220 pounds per 1000 barrels to 8 pounds per 1000 barrels was reported.

A similar system has been described by the Naph-Sol Refining Company in Muskegon, Michigan.[4] Topped crude is emulsified with 4 percent of added water, preheated to 300°F., and settled at 300°F. and at 170 pounds per square inch during 1½ hours. The reduction in salt content received is from about 150 pounds per 1000 barrels in crude oil to 20 pounds per 1000 barrels in treated topped crude.

A patent covers a similar process with an additional stage in which contact with a solid filtering agent occurs.[28]

Chemical treatments for de-salting are generally different from those applied to oil-field emulsions. The reason for this difference probably lies in the fact that only a small expense will be tolerated for a salt-removal process. The Tretolite system is not generally used. The more common reagents employed for de-salting treatments are sodium carbonate, sodium soaps and, perhaps, sodium hydroxide. Stratford, McIntyre, and Moor[29] patented a process in which oil and a sodium-hydroxide solution were mixed, heated under pressure, and settled after reduction of pressure.

As early as 1931 the use of Petroleum Rectifying Company's electrical-dehydration system for salt removal was patented by H. C. Eddy.[30] The first commercial application of this system to salt removal was made in 1935 in Catlettburg, Kentucky,[10, 11, 31] in the refinery of the Ashland Oil & Refinery Company. Crude oil to be treated was heated to 170-180°F., and mixed with previously-heated water. Water equal to about 20 percent of the crude volume was added, and the prepared emulsion was discharged between the two electrodes. A potential difference of 32,000 volts was maintained between these electrodes by an alternating current; 90 to 95 percent removal of salt was obtained when the charged oil contained 220 pounds per 1000 barrels. Hanson[9] states that the electrical de-salting system has been used in a large number of locations on widely-varying crude oils with good success.

Representatives of a number of Mid-Continent refineries using de-salting systems have been willing to describe the systems they have used and the results they have secured. With their consent brief descriptions of the units are being included.

1. During 1937 the system employed in the first refinery consisted essentially of emulsification of crude oil with an aqueous sodium-carbonate solution, heating by heat-exchange, percolation through a packed column, and settling in a horizontal cylinder.

The crude oil was emulsified with 1.5 percent of 0.3 percent sodium-carbonate solution in the charging pump and in heat exchangers, and the latter raised the temperature of the mixture to 200°F. The prepared emulsion then percolated upward through a vertical column packed with graded rock and sand, and was led to a horizontal settler held at a pressure of 25 to 27 pounds per square inch. The total settling time was 50 minutes.

Fairly satisfactory salt removal was accomplished. It was planned that a residual concentration not exceeding 4 to 6 grains per gallon should be maintained. At the present time some changes are being made in the system of operation.

2. The de-salting system installed in the second refinery involves emulsification of the crude oil with an aqueous sodium-carbonate solution and settling after heating.

The emulsion is prepared in the centrifugal charging pump and in heat exchangers, and contains 3 percent of 0.48 percent sodium-carbonate solution. The solution is prepared with soft water-boiler feed water to prevent deposition of calcium carbonate in the lines.

Passage through three heat exchangers raises the temperature of the mixture to 235° F. Finally, the emulsion enters a 600-barrel insulated horizontal settling drum. The time allowed for settling in this vessel is 2 hours. The settler is held at about 235° F., and under a pressure of 80 to 85 pounds per square inch, which is sufficient to prevent any vaporization.

This treatment has resulted in the removal of about 75 percent of the salt. The system lowers the water and sediment from about 0.6 percent to 0.3 percent.

Treatment has raised the carbon-tetrachloride and carbon-disulfide solubilities from 99.4 percent to 99.65 percent, and has reduced the ammonia requirement in the still from 30 pounds per day to 6 pounds per day.

3. In a third refinery a certain amount of treatment was formerly applied to reduce difficulties due to salt. At present no system is in use.

The method previously employed involved emulsification of 0.19 percent of 2.5 percent sodium-carbonate solution, preheating in heat exchangers to 185 to 200° F., settling at this temperature and at a pressure of 80 pounds per square inch for 60 minutes, heating to 300° F. and standing for 50 minutes in a vessel held at 300° F. and at a pressure of 20 to 30 pounds per square inch. Finally the oil passed from this drum to a fractionating column.

It was planned that an aqueous salt solution should settle in and be withdrawn from the first drum. In the second drum, however, conditions were such that boiling occurred. Water distilled, and a part of the salt was expected to settle as a solid, while another part remained colloidally dispersed in dry oil and did not cause deposition or corrosion difficulties.

Sodium soap was used instead of sodium carbonate for a time, and gave less desirable results.

The sodium-carbonate treatment was considered fairly satisfactory, although no very definite knowledge was secured as to the actual results of the treatment.

At present no system for the removal of salt is employed. Rather, it has been found practical to blend a crude of high salt content with one of low content to give a mixture containing less than 20 grams of salt per barrel. Little trouble has been experienced with this mixture.

In addition, controlled preheating and dehydration of crude have resulted in a finely-divided salt that does not cause deposition difficulties.

4. An installation of the Petroleum Rectifying Company's electrical de-salting system has been made in the fourth refinery to be described.

Units are prepared of a size suitable for treating 1500 barrels of oil per day. In operation the crude petroleum is heated to about 160° F. by heat exchange, and is emulsified in a controlled manner with

about 20 percent or less of water which has previously been heated to 160° F. The prepared emulsion is led between two electrodes possessing a potential difference of 33,000 volts, and then passes to a settling zone. An alternating current is used. Settling times of 2 hours or more are provided.

With careful control of conditions it is possible to remove 95 percent of the salt. Reduction of salt to 5 pounds per 1000 barrels and of water and sediment to 1 percent or as low as 0.2 percent is expected.

Thanks are extended to E. R. Jones, Skelly Oil Company, Eldorado, Kansas; R. E. Puckett, Barnsdall Oil Company, Wichita, Kansas; Guy Kirk, Kanotex Refining Company, Arkansas City, Kansas; and C. W. Berger, Globe Oil & Refining Company, McPherson, Kansas, for the information they have given.

EXPERIMENTAL STUDY

In the laboratory study of de-salting, the more promising of the methods for treating oil-field emulsions have been investigated. Studies have been made of settling at normal and elevated temperatures, both with and without the addition of water. Centrifugal treatment has not been considered because of the large cost involved. Prime consideration has been given to other mechanical treatments, for such methods are comparatively cheaply applied. The effects of contact with two solid agents have been observed, and considerable attention has been given to methods for contacting crude oil with added water.

The study of chemical treatment has been confined to one or two reagents. Again, the reason for this restriction of the field is the necessarily low cost of a feasible process.

The electrical methods have not been studied in the laboratory; for this field is well covered with existing patents, and the application of these methods has been widely considered.

The method of treatment deemed most desirable for the crude under consideration from the results of laboratory study involves a combination of chemical treatment (treatment with a sodium-carbonate solution), treatment by contact with a solid agent (excelsior), and settling.

I. THE DETERMINATION OF CHLORIDES IN CRUDE PETROLEUM

The method proposed by R. R. Matthews in 1921[32] for the determination of chlorides has been generally followed. A number of modifications have been made in the procedure, however, and the method actually used is described below.

500 ml. of the crude oil to be tested are transferred to a 3-liter glass-stoppered bottle. 125 ml. of acetone are added, and the bottle is shaken vigorously for 2 minutes. 1375 ml. of distilled water are next added, and the mixture is shaken for an additional 3 minutes. Finally, 2 grams of sodium soap are added, and shaking is continued for another 3 minutes.

The bottle is permitted to stand until the aqueous phase becomes clear—preferably for two or three days. Samples of this phase are then removed with a siphon. To 500 ml. are added 25 ml. of a 20 percent magnesium-nitrate solution. The mixture is made neutral with nitric acid, and an excess of 5 ml. of 50 percent nitric acid are added. An excess of standard silver nitrate is measured in, followed by 5 ml. of ferric-alum indicator, and the excess of silver nitrate is determined by titration with standard potassium thiocyanate. The end point is indicated by the appearance of the red color of ferric thiocyanate.

If 0.1 N solution of silver nitrate ($AgNO_3$) is used, the following relationship applies:

(ml. $AgNO_3 \rightleftarrows$ Cl- in. 500 ml. water) (2.05)
= (grains per gallon of chlorides in oil as NaCl).

In the determination, soap is added to prevent the formation of a stable water-in-oil emulsion. Magnesium nitrate is then added to precipitate the soap before the titration.[33] The Volhard method is used in preference to direct titration with silver nitrate with a potassium-chromate indicator, for a more definite end point is obtained.

The results obtained by this method were easily duplicated. A repeated extraction and a study of a crude of known salt content both indicated practically complete removal of salt in one treatment.

Samples of crude oil used in de-salting experiments were of 37 to 40° API gravity, and of 39 to 40 seconds viscosity (Saybolt Universal) at 100° F.

II. SIMPLE SETTLING EXPERIMENTS

Laboratory de-salting experiments have been conducted with the idea that, while the results are not directly translatable to the results which may be expected on a commercial scale unit, those procedures which are most satisfactory in the laboratory may be expected to be most satisfactory in the plant. A comparison between a given plant operation and the same procedure in the laboratory gives a basis for estimating the value of similar laboratory processes when transferred to a plant scale.

Earliest experiments involved settling of crude oil both at room temperature and at an elevated temperature without the addition of any liquid, with the addition of water and, finally, with the addition of soap and sodium-carbonate solutions.

All experiments were conducted in a continuous manner. If an aqueous liquid was added, the required amount of liquid of the desired concentration was continuously supplied. Oil and water were beaten together during an average time of about 20 minutes by a small glass-bladed stirrer driven at 3000 r.p.m. The prepared emulsion next passed through a pump to a tube furnace and to an insulated electrically-heated settling vessel. The settler was a horizontal cylinder 6 inches in diameter and 14 inches long. Operation of the settler was adjusted to minimize agitation, convection, etc. In each case the settler maintained the oil at the temperature reached in the furnace. Oil entered the settler at the bottom at one end, and was removed at the top of the opposite end. Water was drained from the bottom of the outlet end.

Summaries of a number of experiments are listed in Table 1.

Experiments No. 1 and 2 indicate that simple settling is unsatisfactory. Experiments No. 3 and 4 show that, with the method of emulsification used, an emulsion formed from water alone is not satisfactorily resolved by simple settling. Later experiments demonstrate that either sodium-carbonate solutions or solutions of commercial sodium soap give emulsions which are more readily resolved than emulsions made with water alone.

The efficiency of salt removal in each of these cases was too poor for practical application of the

TABLE 1
Simple Settling Experiments

Experiment No.	Settling Conditions: Temperature (° F.)	Settling Conditions: Time (Minutes)	Added Liquid	Amount of Added Liquid (Percent by Volume)	Pressure (Lb. per Sq. In., Gage)	Sodium-Chloride Concentrations (Grains per Gallon): Original	Sodium-Chloride Concentrations (Grains per Gallon): Final	Removed (Percent)
1	86	60	.....	....	....	11.36	11.20	1.4
2	155	70	.....	....	....	9.67	9.35	3.3
3	80	74	Water.....	1.78	....	11.4	10.4	8.8
4	163	73	Water.....	1.5	....	13.0	11.5	11.5
5	185	75	Sodium-soap solution (2 grams per liter).....	1.53	10	9.45	7.8	17.5
6	186	76	Sodium-carbonate solution (5 grams per liter).....	1.56	10	11.43	8.6	24.7
7	205	77	Sodium-carbonate solution (2.5 grams per liter).....	3.16	14.2	10.1	7.2	28.7
8	201	80	Solution of soap (2 grams per liter) and sodium carbonate (5 grams per liter).....	1.64	14	10.2	8.8	13.7
9	300	80	Sodium-carbonate solution (5 grams per liter).....	1.64	14	9.0	7.5	16.7

method. The results indicate, however, that a sodium-carbonate solution possesses decided advantages over water as a de-salting agent.

III. METHODS FOR CONTACTING OIL AND WATER

In the experiments just described a uniform method was used for obtaining contact between oil and added water. When that method was employed, the means considered were insufficient to cause separation of the added water and so of dissolved salts.

Two possible lines of attack present themselves. The emulsion may be formed as above, and a search may then be made for a method of breaking this emulsion. This general system is described in a later section. As an alternative, an attempt may be made to remove salt without as intimate contact as was secured in early experiments. This method of approach has been used also.

If oil and water are mixed sufficiently gently, very rapid separation of phases occurs, but practically no salt is removed. On the other hand, if added water is very closely emulsified, then all salt will be present in the added water; but this water will be difficult to separate. At some point between these extremes all or a large part of the salt will be found in the added water, and the emulsion will still be comparatively unstable. It remains to determine whether, with this optimum method of contacting oil and water, the phases are decidedly more easily separated than with the method of contacting described in previous experiments. If the separation does occur readily, this contacting system may be used in conjunction with a comparatively mild treatment for breaking the emulsion, and a satisfactory salt separation will be secured.

Experiments No. 10 and 11 (Table 2) represent opposite extremes in this series of possible methods of contacting. The data for No. 10 indicate 95 percent transfer of salt to added water, but only 39 percent of this added water was removed. In No. 11 a complete separation of added water occurred, but only a negligible removal of salt was obtained. Microscopic examination of the emulsion in No. 10 indicated that the largest particles in the prepared emulsion were of about twice the diameter of the largest particles in the original crude oil.

The next experiments were concerned with a different method for mixing oil and water. It was believed that if oil and water were continuously contacted without a dispersion of either phase in the other in the form of small droplets, a satisfactory removal of salt might be accomplished without the formation of a stable emulsion at any time.

In the first arrangement used the stream of charged crude oil entered a vessel containing both oil and water layers. One phase was repeatedly washed through the other for 30 minutes. Then oil from the crude-oil layer, with any suspended water, was pumped through a heat exchanger to a settler. The apparatus was similar to that described previously except for the contacting device.

The washing action was secured with a pumping

TABLE 2
Extreme Methods for Contacting Oil and Water

	Experiment No. 10	Experiment No. 11
Added liquid	Distilled water	Distilled water
Amount of added liquid, percent by volume	100	100
Contact	Stirring for 30 min. (with blade at 3,000 r.p.m.)	Flow together through furnace
Settling temperature, ° F.	204	205
Settling time, min.	71	120
Pressure on system, lb. per sq. in., gage	13	16
Original sodium-chloride concentration, grains per gallon	5.6	7.0
Final sodium-chloride concentration, grains per gallon	3.5	6.75
Sodium chloride removed (by chloride analysis of oil) percent	38	3.6
Sodium chloride removed (by chloride analysis of water) percent	37	2.75
Added water separated, percent	39.2	100

TABLE 3
Effects of a Washing Action at Room Temperature

	Experiment No. 12	Experiment No. 13
Added liquid	100 percent water	100 percent water
Contact	Water through oil	Oil through water
Settling temperature, ° F.	200	210
Settling time, min.	75	80
Pressure on system, lb. per sq. in., gage	10	16
Original sodium-chloride concentration, grains per gallon	8.3	8.3
Final sodium-chloride concentration, grains per gallon	7.1	5.5
Sodium chloride removed, percent	14.5	33.7

TABLE 4

Effects of Washing with Water at an Elevated Temperature

	Experiment No. 14	Experiment No. 15
Added liquid	Water	Water
Contact	Oil through water (700 r.p.m.)	Oil through water (1,560 r.p.m.)
Temperature at entrance to mixer, ° F.	240	275
Temperature at entrance to settler, ° F.	185	198
Temperature of settler, ° F.	203	201
Time in mixer, min.	20	20
Settling time, min.	81	80
Pressure on system, lb. per sq. in., gage	18	26
Original sodium-chloride concentration, grains per gallon	7.67	10.4
Final sodium-chloride concentration, grains per gallon	5.7	6.7
Sodium chloride removed, percent	25.6	35.6
Water and sediment in treated oil, percent	0.42	6.0

TABLE 5

Effects of Washing with Sodium-Carbonate Solution at an Elevated Temperature

	Experiment No. 16	Experiment No. 17	Experiment No. 18
Added liquid	Sodium-carbonate solution (5 grams per liter)	Sodium-carbonate solution (5 grams per liter)	Sodium-carbonate solution (5 grams per liter)
Contact	Water through oil (1,200 r.p.m.)	Water through oil (1,560 r.p.m.)	Oil through water (1,560 r.p.m.)
Temperature at entrance to mixer, ° F.	250	275	270
Temperature at entrance to settler, ° F.	185	197	200
Temperature of settler, ° F.	203	204	203
Time in mixer, min.	20	20	20
Settling time, min.	80.5	80	79.5
Pressure on system, lb. per sq. in., gage	15	25	22
Original sodium-chloride concentration, grains per gallon	6.27	7.8	9.1
Final sodium-chloride concentration, grains per gallon	1.87	6.0	1.6
Sodium chloride removed, percent	70	23	82.4
Water and sediment in treated oil, percent	0.306	1.6	0.42

stirrer. This stirrer consisted of a shaft bearing three sets of three propeller blades. The shaft, with attached blades, operated in a cylindrical barrel which was closed except for openings near each end. The stirrer and mixing vessel were so arranged that the lower openings in the stirrer barrel were near the bottom of the mixing vessel and the upper openings were just below the surface of the liquid. This stirrer could be driven in either direction, and its action was to deliver a continuous stream of one phase and distribute it through the other phase. The speed of rotation of the stirrer determined the speed of this mixing stream. An arrangement was provided to maintain the oil-water interface near the center of the mixing vessel.

In experiments No. 12 and 13 this system was used. In one case oil washed through water, and in the other the reverse operation was employed. In each case an attempt was made to use the maximum rate of washing which did not result in excessive emulsification. The data are given in Table 3. In No. 13 oil entered the settler by bubbling through a layer of water, while in No. 12 this was not the case.

The data in Table 3 indicate that washing oil through water is preferable to the reverse operation.

TABLE 6

Effects of a Variation in the Concentration of Washing Solution

	Experiment No. 19
Added liquid	Sodium-carbonate solution (2.5 grams per liter)
Contact	Oil through water (1,560 r.p.m.)
Temperature at entrance to mixer, ° F.	275
Temperature at entrance to settler, ° F.	195
Temperature of settler, ° F.	202
Time in mixer, minutes	20
Settling time, minutes	80
Pressure on system, lb., per sq. in., gage	25
Original sodium-chloride concentration, grains per gal.	7.8
Final sodium-chloride concentration, grains per gal.	2.2
Sodium chloride removed, percent	72
Final water and sediment in treated oil, percent	1.0

This point was to be expected, for the emulsion which tends to form possesses water as the internal phase.

Many considerations indicated that the washing action would be more effective if conducted at a higher temperature. Therefore, ensuing experiments were made with a modified apparatus.

In the new assembly oil and any aqueous solution were fed directly to the pump. This mixture then passed through the heat exchanger, was heated to the temperature chosen, and entered the bottom of the mixing vessel.

Mixing occurred in a vertical cylinder 11 inches high and prepared from a piece of 4-inch pipe. The pumping stirrer described above was mounted within this chamber, and driven through a packed bearing in the top of the drum. The vessel was so arranged that, during operation, it remained about half full of water and half full of oil. Oil from the mixer passed to the bottom of the settler previously described.

The data in Table 4 give the effects of washing oil through water at an elevated temperature. In No. 14 the rate of mixing was nearly correct. In No. 15 excessive emulsification was encountered. The salt removal accomplished in No. 14—with a near-optimum method of contacting—was, however, very poor. Further experiments involved the use of various sodium-carbonate solutions, and a portion of these is summarized in Table 5.

Experiments No. 16 and 17 give the effect of speed of washing. The rate in No. 16 was apparently optimum. Comparisons of No. 18 with No. 16 and 17 substantiates the idea that a greater violence of mixing can be tolerated when oil is washed through water, and a better salt removal is accomplished. Comparison of Table 5 with Table 6 very definitely indicates the benefit derived through use of sodium carbonate.

One experiment was made with a sodium-carbonate solution of lower concentration, and the results

are summarized in Table 6. In this experiment the efficiency of salt removal very definitely increased as salts accumulated in the extracting solution. At the same time water and sediment fell. The experiment was not continued until these values became constant.

A comparison of No. 19 with No. 15 and 18 places a solution of intermediate concentration in an intermediate position as regards efficiency of action. However, there is a definite indication that some concentration below 5 grams per liter is most desirable—when the cost of reagent is considered.

The experiment just described were all conducted with a comparatively large amount of solution, and indicated the results which could be obtained without regard to the amount of solution required.

One final experiment was made just as before, but was continued for a longer period of time. The idea was held that, as chlorides accumulated in the extracting solution, the efficiency of salt removal would first increase; and then, as the chloride concentration increased further, would decrease. A knowledge of the highest chloride concentration corresponding to satisfactory salt removal would enable calculation of the replenishing solution necessary to maintain this efficiency. The data secured from the experiment are given in Table 7.

At the close of experiment No. 20 it was found that a certain amount of emulsion of high-water content had formed and remained in the settler. This had removed a large part of the water phase from the mixer, and so probably accounted for part of the decrease in efficiency with time in the experiment. The run indicated, then, that less than 3 percent of 0.3 percent sodium-carbonate solution need be added continuously to effect the removal of 70 percent of the salt. It is probable that the amount would be decidedly less than this.

Another, longer experiment would be necessary to determine whether, with additional accumulation of water-rich emulsion in the settler, the discharged oil would finally have a high content of water and sediment. With increased time the rate of resolution of this emulsion might become equal to its rate of formation. Inasmuch as another procedure which seemed more desirable was developed, this additional study was not made.

In experiments involving the washing action with rotation of the stirrer at 1560 r.p.m., each sample of oil was washed through the water phase 260 times during its 20 minutes in the mixer.

IV. SALT REMOVAL THROUGH CONTACT OF AN EMULSION WITH A SOLID AND SETTLING

As previously outlined, two general systems of de-salting may be used. An attempt may be made to remove salt without the formation of an emulsion. The experiments last described were of this nature. On the other hand, an emulsion may be intentionally-prepared, and special means may then be sought to resolve this emulsion. The remaining experiments pertain to treatment with a solid agent as a special means for resolving an intentionally-prepared emulsion.

An early simple experiment involved pumping cold untreated crude oil through a small column packed with excelsior. The column consisted of an 18-inch section of 3-inch pipe. The pipe was capped at the top, and oil entered through this cap. Excelsior was packed in the pipe section. Below this was a 3-inch

TABLE 7

A Long Experiment Involving Washing with a Sodium-Carbonate Solution

	Experiment No. 20
Added liquid	Sodium-carbonate solution (3.3 grams per liter)
Contact	Oil through water (1,560 r.p.m.)
Temperature at entrance to mixer, ° F	280
Temperature at entrance to settler, ° F	203
Temperature of settler, °F	202
Mixing time, minutes	20
Settling time, minutes	80
Pressure on system, lb., per sq. in., gage	25
Duration of experiment, hours	75
Volume of crude charged, liters	225

	Salt Concentration			Water and Sediment	
	Original	Final	Removed	Original	Final
	(Grains per Gal.)		(Percent)	(Percent)	
1st 5 hours	9.7	2.3	76	0.26	0.63
2nd 5 hours	8.8	1.4	84	0.25	0.40
3rd 5 hours	8.7	1.4	84	0.26	0.26
4th 5 hours	8.7	1.6	82	0.29	0.44
5th 5 hours	8.5	1.7	80	0.15	0.55
6th 5 hours	8.1	2.3	72	0.25	0.46
7th 5 hours	8.1	2.1	74	0.26	0.41
8th 5 hours	8.2	2.9	65	0.28	0.45
9th 5 hours	10.5	3.4	68	0.35	0.59
10th 5 hours	11.9	3.5	71	0.30	0.43
11th 5 hours	11.4	4.3	62	0.35	0.50
12th 5 hours	10.7	4.4	59	0.32	0.58
13th 5 hours	9.8	4.1	58	0.32	0.51
14th 5 hours	9.3	4.9	47	0.32	0.46
15th 5 hours	8.9	4.6	48	0.25	0.47

tee. Any water collected was drained from the bottom of the tee, and treated oil was discharged from the side. The space within the tee was open; so a small settling zone was present. After the pipe section was packed, 1260 ml. of water could be placed in the voids in the excelsior. The open space in the tee contained an additional 500 ml.

Before an experiment, this column was always soaked with a chloride solution to prevent any erroneous results due to a mere absorption of water. Such a column acts to cause coalescence of water droplets, and not as a filter or absorbent.

When crude oil was pumped through the column at 100° F. and with a time of contact of 12.5 minutes, a salt removal of 19.2 percent was secured.

Inasmuch as the excelsior acts to cause coalescence of drops rather than actually to remove water, later experiments employed a settler in conjunction with the excelsior column. Any added water was emulsified with the oil by a blade revolving at 3000 r.p.m. as in experiment No. 3. The emulsion was heated by heat exchange to the desired temperature, passed from the top down through the packed column, and led from the side of the tee at the bottom to the bottom of one end of a horizontal settling drum. Dry oil was withdrawn from the top of the other end of this drum.

In Table 8 are listed results with both the excelsior column described and with a sand column. The sand column was made with 14- to 20-mesh sand, and in the same piece of pipe used for excelsior. The over-all volumes of the two colums were thus the same. The volume of the voids was but 900 ml. in the case of the sand column.

Comparisons of No. 21 and 22 with No. 4 and 6 indicate the great benefit obtained through the use of the excelsior column. Comparison of No. 21 and 22 with No. 23 and 24 shows that excelsior is definitely more effective than 14- to 20-mesh sand. The

TABLE 8

Comparison of Excelsior- and Sand-packed Columns

	Experiment No. 21	Experiment No. 22	Experiment No. 23	Experiment No. 24
Packing material	Excelsior	Excelsior	Sand	Sand
Added liquid	Sodium-carbonate solution (3 grams per liter)	Water	Sodium-carbonate solution (3 grams per liter)	Water
Amount of added liquid, percent by volume	1.42	3	1.42	3
Temperature at entrance to column, ° F.	205	205	220	230
Temperature at entrance to settler, ° F.	155	165	135	152
Temperature of settler, ° F.	201	202	201	203
Time in packed bed, min.	25	25	18	18
Time in settler, min.	80	110	80	110
Pressure on system, lb. per sq. in., gage	20	25	28	28
Original sodium-chloride concentration, grains per gallon	11.4	10.8	9	9.2
Final sodium-chloride concentration, grains per gallon	4.4	2.4	4.4	3.7
Sodium chloride removed, percent	61.3	78	51	60
Water and sediment in treated oil, percent	0.46	0.62	0.48	0.97
Water and sediment in original oil, percent	0.35	0.33	0.33	0.30

great density of sand, the small percentage of voids, the packing tendency, and the high pressure drop through any bed are all factors hindering the practical use of sand as a contact agent. Inasmuch as it was considered that excelsior presented advantages in every respect, further experiments were concerned with the use of the previously-described excelsior column.

TABLE 9

The Effect of Time of Treatment with Excelsior

	Experiment No. 25
Added liquid	Sodium-carbonate Solution (3 grams per liter)
Amount of added liquid, percent by volume	1.42
Temperature at entrance to column, ° F.	220
Temperature at entrance to settler, ° F.	153
Temperature of settler, ° F.	201
Time in excelsior bed, minutes	50
Time in settler, minutes	80
Pressure on system, lb., per sq. in., gage	20
Original sodium-chloride concentration, grains per gal.	9.0
Final sodium-chloride concentration, grains per gal.	2.7
Sodium chloride removed, percent	70
Water and sediment in treated oil, percent	0.35
Water and sediment in original oil, percent	0.29

Experiment No. 25 (Table 9) was conducted to determine the effect of the time of contact between excelsior and oil. The rate was reduced to half that given in No. 21, but otherwise this experiment was duplicated. As anticipated, the prolonged treatment resulted in an improvement in salt removal and in a decrease in water and sediment. The improvement, however, through prolonged treatment is not sufficiently great to justify the use of equipment of double size.

The next five studies were made with two volume percentages of water and with four temperatures. The experiments were made to determine the effect of temperature on the completeness of salt and water removal. Results are given in Table 10.

Comparison of No. 26 with No. 28 indicates that the addition of 5 percent of water is less desirable than the use of 3 percent—both from the standpoint of salt removal and of water and sediment. Experiments No. 27 to 30 demonstrate the effect of temperature. The percentage of salt removed increases, and the water and sediment decreases as the temperature rises. It is noteworthy, however, that most of the change occurs between 100 and 200° F., and 200° F. is almost as satisfactory as 275° F.

In the preceding experiments (No. 27 to 30) a large portion of the added water appeared finally as a very viscous water-rich emulsion in the bottom of the settler. Those experiments were not sufficiently long that this deposition caused any particular difficulty. Experiment No. 31 (Table 11) was undertaken to determine whether this emulsion would eventually resolve as quickly as formed or would accumulate to prevent satisfactory settling. It is to be noted that, as the experiment proceeded, the efficiency of salt removal decreased, and the residual water content of treated oil rose. The subsidence of water particles was never very satisfactory, but the removal became less successful as a viscous emulsion of high water content accumulated in the settler.

Inasmuch as sodium-carbonate solutions yield emulsions which are comparatively readily resolved, the final experiment, No. 32 (Table 12), was a duplication of No. 31 with the use of sodium carbonate. This experiment resulted in satisfactory salt removal, and indicated successful continued operation. The high percentage removal of salt and the low water content of discharge oil proved satisfactory extraction and settling of water from the oil phase.

The quantity of water removed was encouraging. While this amount did not equal the quantity charged, the percentage of charged water removed continued to increase as the experiment progressed; i. e., there was an accumulation of emulsion rich in water, but the rate of resolution of this emulsion approached the rate of formation.

TABLE 10

The Effect of Temperature of Treatment with Excelsior

	Experiment No. 26	Experiment No. 27	Experiment No. 28	Experiment No. 29	Experiment No. 30
Added liquid	Walnut River water	Walnut River water	Walnut River water	Walnut River water	Walnut River water
Amount of added liquid, percent by volume	5	3	3	3	3
Temperature at entrance to column, ° F.	203	100	200	240	268
Temperature at entrance to settler, ° F.	205	100	203	245	277
Temperature of settler, ° F.	208	99	212	250	284
Time in excelsior bed, min.	20	20	20	20	20
Time in settler, min.	36	36	36	36	36
Pressure on system, lb. per sq. in., gage	22	11	30	60	72
Original sodium-chloride concentration, grains per gallon	8.0	7.5	7.6	5.7	7.0
Final sodium-chloride concentration, grains per gallon	3.2	5.6	2.3	1.6	1.9
Sodium chloride removed, percent	60	25	70	72	73
Water and sediment in treated oil, percent	1.2	1.6	0.77	0.75	0.58
Water and sediment in original oil, percent	0.28	0.26	0.25	0.26	0.25

TABLE 11

A Long Experiment with Addition of Water Alone

	Experiment No. 31
Added liquid	Walnut River Water
Amount of added liquid, percent by volume	3
Temperature at entrance to column, ° F	250
Temperature at entrance to settler, ° F	250
Temperature of settler, ° F	250
Time in excelsior bed, minutes	20
Time in settler, minutes	49
Pressure on system, lb., per sq. in., gage	75
Duration of experiment, hours	33⅓
Volume of oil charged, liters	100.5

	Sodium-Chloride Concentration			Water and Sediment	
	Original	Treated		Original	Treated
	(Grains per Gallon)		Removed (Percent)	(Percent)	
1st 3 hours	11.4	6.8	40	0.27	1.6
2nd 3 hours	11.7	4.5	61	0.30	0.88
3rd 3 hours	11.6	4.0	66	0.30	1.08
4th 3 hours	12.2	5.5	55	0.25	1.25
5th 3 hours	11.3	5.8	49	0.30	1.22
6th 3 hours	10.4	5.4	48	0.28	1.19
7th 3 hours	11.0	5.6	49	0.25	1.05
8th 3 hours	11.4	5.2	54	0.30	1.03
9th 3 hours	10.0	6.2	38	0.25	1.23
10th 3 hours	9.6	5.7	41	0.29	1.53
11th 3 hours	9.4	5.6	41	0.30	1.47

DISCUSSION

In the search for the most desirable de-salting system for this crude oil, attention may be returned to a consideration of de-salting units which have been described in the literature, and of those which have been visited in the Mid-Continent area.

Literature references describe satisfactory de-salting, following emulsification of water and settling, in refineries in Alma and Muskegon, Michigan. Temperatures of 250 and 300° F. were employed. While these conditions were not exactly duplicated, all of the experimental results above indicate that the crude oil used cannot be satisfactorily de-salted by simple emulsification of water and settling. It is very probable that the treatment necessary for oil supplied to the Michigan refineries mentioned differs from that necessary for the oil supplied here.

In the case of the second Mid-Continent refinery described above, satisfactory salt removal followed emulsification of 3 percent of 0.5-percent sodium-carbonate solution and settling for 2 hours. Laboratory experiments roughly parallel the results secured. Experiments with simple settling failed to give satisfactory removal, but conditions were always comparatively mild. Experiments Nos. 16, 17, and 18, involving a washing action gave good salt removal. If as good extraction could be obtained without the washing action, the method employed in the refinery considered might well be applicable to the crude oil studied in the laboratory. The settling time used in the plant installation was long, and large vessels were required.

In the third commercial unit described a part of the salt was removed, but a large part remained in suspension in a form which did not cause deposition difficulties. Such a system is not applicable when the solubility of asphalt is of prime importance.

In another refinery oil is mixed with 1.5 percent of 0.3-percent sodium-carbonate solution, heated, passed through a sand-packed column, and settled. Operation is fairly satisfactory. Comparison with a similar laboratory treatment shows approximately the same efficiency of salt removal. Thus, a study of commercial results indicates that the efficiencies obtained in the laboratory would be roughly duplicated in the plant in units with the same times of contact or settling.

Laboratory studies with emulsification of 3 percent of 0.3-percent sodium-carbonate solution, passage through an excelsior column, and settling gave more complete salt removal than similar experiments with smaller amounts of solution and contact with sand in a packed column.

After this comparison of Mid-Continent de-salting units and correlation of their systems with laboratory results, we may well review the points brought out in the experimental studies.

Simple settling of crude oil at normal or elevated temperatures does not suffice to remove salt unless an uneconomically-long settling period is provided. Likewise, settling after the emulsification of added water is unsatisfactory. In this case it is difficult to say that the method is impossible, for any number of procedures for contacting oil and water may exist.

If sodium carbonate is dissolved in emulsified water,

TABLE 12

A Long Experiment with Addition of Sodium-Carbonate Solution

	Experiment No. 32
Added liquid	Sodium carbonate in Walnut River Water (3 grams per liter)
Amount of added liquid, percent by volume	3
Temperature at entrance to column, ° F	250
Temperature at entrance to settler, ° F	250
Temperature of settler, ° F	250
Time in excelsior bed, minutes	20
Time in settler, minutes	49
Pressure on system, lb., per sq. in., gage	81
Duration of experiment, hours	102⅔
Volume of oil charged, liters	308

Chloride Removal:

	Average Values of Sodium-Chloride Concentration		
	Original Oil	Treated Oil	Removed (Percent)
	(Grains per Gallon)		
1st 20 hours	9.6	1.5	84.3
2nd 20 hours	8.1	1.36	83.3
3rd 20 hours	7.34	1.17	84.2
4th 20 hours	8.42	1.62	80.8
5th 20 hours	9.72	1.84	81.0

Average Water and Sediment:

	Original Oil (Percent)	Treated Oil (Percent)
1st 20 hours	0.26	0.30
2nd 20 hours	0.25	0.25
3rd 20 hours	0.24	0.11
4th 20 hours	0.27	0.27
5th 20 hours	0.31	0.35

Water Removal (Average Values):

	Water Added	Water Removed			Percentage of Added Water Removed
		Excelsior Column	Settler	Total	
	(Milliliters)				
1st 10 hours	900	490	25	515	57.3
2nd 10 hours	900	620	...	620	69.0
3rd 10 hours	900	503	110	613	68.2
4th 10 hours	900	237	354	591	65.8
5th 10 hours	900	136	442	578	64.3
6th 10 hours	900	92	501	593	66.0
7th 10 hours	900	68	507	575	64.0
8th 10 hours	900	55	533	588	65.5
9th 10 hours	900	60	573	633	70.5
10th 10 hours	900	57	590	647	72.0

the subsidence of emulsified particles and the coalescence of separated drops are more rapid than when water alone is employed. The effect becomes more pronounced as the concentration of sodium carbonate increases from 2.5 to 5 grams per liter.

The agitation present in a body of boiling oil is sufficient essentially to prevent settling. It is possible that a very mild ebullition would favor coalescence of drops.

If oil and a sodium-carbonate solution are mixed by washing one liquid through the other, an efficient salt extraction can be obtained with very little emulsion formation. The effect is better if oil is washed through water than with the reverse operation, for the emulsion which tends to form is one with water in the internal phase.

The separation of an emulsified water phase occurs more readily when this phase contains some extracted chlorides.

Passage of an emulsion through a column packed with excelsior has a decided tendency to resolve the emulsion. An excelsior packing is preferable to a packing of the same size of 14- to 20-mesh sand. The beneficial effects of sodium carbonate are again observed in settling following passage through a packed column.

Contact with excelsior for 25 minutes is nearly as effective in resolving an emulsion as contact for twice this time.

In a process involving passage of an emulsion of oil and water through a packed column and settling the desirable amount of added liquid is about 3 percent. The efficiency of salt removal increases as the temperature rises from 100 to 270° F. The greatest increase comes, however, between 100 and 200° F., and results at 200° F. are nearly as satisfactory as those at 270° F.

It is probable that, following use of a packed column, some settling time is very beneficial; but that, as this settling time is increased, the benefit derived from the extension decreases. In other words, a settling period of medium length is most economical.

Most satisfactory and successful laboratory de-salting was secured by emulsification of 3 percent of 0.3-percent sodium-carbonate solution, passage through an excelsior column at 250° F. during 20 minutes, and settling of 50 minutes at 250° F.

From the laboratory study, two generally-successful methods of salt removal developed. To duplicate the conditions of experiment No. 20 on a commercial scale (assuming 10,000 barrels of oil a day) the mixing vessel would contain 320 barrels and the settler's volume would be 550 barrels. Water consumption would be less than 13,000 gallons a day, and less than 350 pounds of soda ash would be required in a day. It is estimated that the power necessary to give the re-circulation provided in the laboratory would cost $7.40 a day for this unit, but it is probable that a smaller re-circulation ratio would suffice in the plant.

To duplicate No. 32 on a plant scale 3 percent of an 0.3-percent sodium-carbonate solution is introduced into the crude-oil stream on the suction side of the crude-oil charging pump. Emulsification occurs in the pump and in heat exchangers. The oil-water mixture is heated by heat exchange to 250°F., led to an excelsior-packed column, and then to a settler. The packed column has a volume of 290 barrels (for 10,000 barrels a day) and the settler contains 340 barrels.

Operation involves the use of 13,000 gallons of soft water and 320 pounds of soda ash in a day. Inasmuch as the excelsior does not act as a filter, it should require replacement but rarely. This second method of operation is preferred because of a lower cost of operation.

SUMMARY

1. De-salting systems in use in several Mid-Continent refineries have been described.

2. Satisfactory salt removal may be accomplished by repeatedly washing oil through a sodium-carbonate solution at 200°F. during 20 minutes and settling at this temperature for 80 minutes. Less than 3 percent of 0.3-percent sodium-carbonate solution need be added continuously.

3. A system of treatment involving emulsification of 3 percent of 0.3-percent sodium-carbonate solution, percolation of the mixture through an excelsior column at 250°F. during 20 minutes, and settling at 250°F. for 50 minutes results in the removal of 80 percent of the salt present in crude oil.

4. A comparison of results obtained in the laboratory with those obtained in plant operation indicates that results from a laboratory study should be approximately duplicated in the plant.

5. Application of the most satisfactory laboratory treatment in the refinery involves use of a 290-barrel container as a packed column and of a 350-barrel drum as a settler for each unit processing 10,000 barrels a day; 13,000 gallons of water and 320 pounds of soda ash are required each day for each unit.

6. A mineral bed (14- to 20-mesh) is less effective than a corresponding excelsior bed for resolving a crude-oil emulsion.

BIBLIOGRAPHY

[1] D. B. Dow, "Oil-Field Emulsions," *U. S. Bur. Mines, Bull. 250.*
[2] E. R. Jones, *Refiner Natural Gasoline Mfr.* **16** [5] 208 (1937).
[3] C. H. M. Roberts, *Petroleum Eng.* **8** [6] 57 (1937).
[4] *Refiner Natural Gasoline Mfr.* **16** [5] 206 (1937).
[5] K. S. Valentine and G. MacLean, *Refiner Natural Gasoline Mfr.* **14** [1] 32 (1935).
[6] M. J. Leahy, *Refiner Natural Gasoline Mfr.* **16** [2] 88 (1937).
[7] L. C. Uren, *Natl. Petroleum News* **21** [13] 51 (1929).
[8] D. H. Fortine, *Oil Gas J.* **35** [11] 71 (1936).
[9] G. B. Hanson, *Refiner Natural Gasoline Mfr.* **16** [5] 211 (1937).
[10] *Natl. Petroleum News* **29** [25] 54 (1937).
[11] Allen S. James, *Natl. Petroleum News* **29** [28] R-42 (1937).
[12] *Refiner Natural Gasoline Mfr.* **15** [12] 582 (1936).
[13] William Clayton, *The Theory of Emulsions and Their Technical Treatment*, P. Blakiston's Son and Co., Philadelphia (1935).
[14] D. H. Fortine, *Oil Gas J.* **35** [12] 42 (1936).
[15] U. S. Patent 1,726,309.
[16] Khaduizhi G. Maksimovich, *Novosti Tekhniki Neftedosbuichi* **4** [5] 6 (1936).
[17] U. S. Patent 1,826,276.
[18] U. S. Patent 1,886,293.
[19] U. S. Patent 1,921,751.
[20] U. S. Patent 2,051,226.
[21] U. S. Patent 1,856,156.
[22] U. S. Patent 2,014,936.
[23] U. S. Patent 1,811,177.
[24] U. S. Patent 1,993,646.
[25] French Patent 794,711.
[26] U. S. Patent 1,834,940.
[27] U. S. Patent 1,984,903.
[28] U. S. Patent 1,901,228.
[29] U. S. Patent 1,838,031.
[30] U. S. Patent 1,825,309.
[31] J. J. Allinson, *Oil Gas J.* **36** [4] 65 (1937).
[32] R. R. Matthews, *Ind. Eng. Chem.* **13** 325 (1921).
[33] R. C. Griffin, *Technical Methods of Analysis*, 374, McGraw-Hill Book Co., New York (1927).
[34] F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, John Wiley and Son, Inc., New York, 705 (1919).
[35] F. L. Horine, *Oil Gas J.* **36** [2] 62, 64 (1937).
[36] G. W. Baron van Dedem, *Oil Gas J.* **36** [13] 65-8 (1937).
[37] G. Egloff, E. F. Nelson, C. D. Maxutov, and C. Wirth III, *Oil Gas J.* **36** [22] 57-8, 63; **36** [23] 66, 69-73 (1937).

Laboratory Control *of the* Corrosion of Distillation Equipment *and of* De-salting Processes

L. L. DAVIS, J. M. JONES *and* C. A. NEILSON,
Continental Oil Company

PRACTICAL methods of studying and combating the corrosion of refinery distillation equipment are discussed. The inter-relationship of the various factors causing corrosion and means of combating them are outlined. Detailed methods of test are given for the determination of salt in crude and the amount of corrosives which will be released upon distillation. The use of the pH ‡ value of condensate as a basis for corrosion control, and the relationship between pH, quantity of corrosives present, and the rate of corrosion are discussed. The procedure of using the given methods for the control of corrosion is illustrated by two examples of commercial distillation operations.

This paper was presented at Eighth Mid-Year Meeting, American Petroleum Institute, Lassen Hotel, Wichita, Kansas, May 24, 1938.

A SURVEY of recent refinery trade literature shows a very active interest in the subjects of de-salting crude and the protection of distilling equipment from corrosion. In general, the literature is restricted to descriptions of methods and processes which are limited to certain specific conditions. Inasmuch as it is impossible to translate data from these limited methods and processes for general application, decided differences of opinion have arisen as to the optimum conditions for protection against corrosion. Moreover, the problem is further complicated by the lack of uniformity in the various test methods and control methods employed by the different investigators. During the past 12 years, since Walter Miller[1] discussed our procedure in combating corrosion resulting from Amarillo crude, we have developed uniform methods of studying and combating corrosion at our various refineries. It has been suggested that we present a discussion of these methods as a start toward the accumulation and possible unification of proceedings for the prevention of corrosion of distilling equipment.

Salt in crude oil continues to be one of the most serious problems of the oil refiner. These salts, usually the chlorides of sodium, calcium, and magnesium, cause two different types of trouble: 1, the mechanical clogging of furnaces, tubes, condensers, lines, etc., by deposition; and 2, corrosion of refinery equipment by hydrolysis of some of these salts to chemically-active hydrogen chloride. The clogging of lines may be reduced or entirely eliminated by de-salting the crude oil, which in turn reduces the degree of corrosion; therefore, de-salting and corrosion protection of distillation equipment are so inter-related that both factors must be considered together.

CORROSION OF DISTILLATION EQUIPMENT

The causes of corrosion of distillation equipment and the factors to be considered in the development of means of combating such corrosion may be outlined as follows:

A. Most frequent causes of corrosion:
1. Hydrogen chloride which results from the hydrolysis of magnesium chloride and hydrogen chloride in crude oil from the hydrochloric-acid treatment of wells.
2. Hydrogen sulfide from the crude oil and from the decomposition of organic sulfur compounds.
3. Sulfur dioxide from the decomposition of the products of sulfuric-acid treatment of distillates.
4. Dissolved oxygen, usually from distillation steam.
5. Organic acids, mercaptans, etc. The amount of corrosion from this source is usually negligible.
6. Water corrosion of cooling and condensing coils.

B. The study of any given distillation system to develop corrosion protective measures should include:

1. Determination of which of the above six causes of corrosion must be counteracted.
2. Determination of amount of corrosive agents either formed or released in the system:
   a. By analysis of the charge.
   b. By analysis of the effluent streams.
3. Determination of the extent of metal corrosion:
   a. By analysis of effluent streams.
   b. By record of metal loss from specific plant equipment over a period of time.
4. The selection and control of methods of combating corrosion.
   a. Removal of source of corrosion from oil before charging.
   b. Protective chemical control:
      (1) By stoichiometric calculation of amount required to neutralize corrosives.
      (2) By analysis of effluent stream to determine the nature and amount of corrosive action.
      (3) By the reactivity of the condensate—such as pH value of water.
   c. Use of special alloys in equipment fabrication.
   d. Flooding with water.

‡ Hydrogen-ion concentration.

The successful protection of a given distillation unit from corrosion may include any one or all of the corrosion-combating methods outlined above.

In the study of any corrosion problem the direct relationships are immediately apparent between the three general variables which are: *a*, source, kind, and quality of corrosive material; *b*, the protective method or methods which may be employed; and *c*, the nature of the metals or alloys employed in fabricating the equipment. Obviously, the over-all system is so complex, and the factors are so inter-related, that a discussion of any individual factor would be of little value. Corrosion-prevention studies necessitate the methodical and simultaneous study of all of these inter-related factors.

To give a general idea of the procedure we employ in making a study of a corrosion problem, two typical distillation operations and the corrosion-prevention methods adopted are described. The details of laboratory test procedures are included as an appendix.

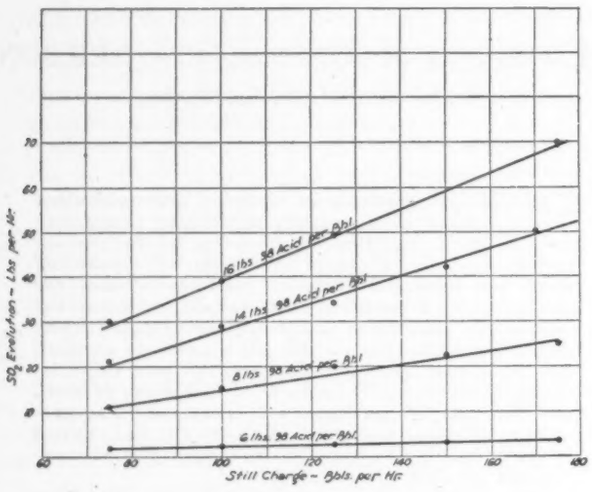


FIGURE 1

The first example of a typical distillation operation involves the relatively simple system of distillation of an acid-treated cracked distillate. In this system sulfur dioxide is the only corrosive agent present, and iron (steel and cast iron) is the only metal exposed to the sulfur dioxide. The second example pertains to a more complex crude distillation system in which two corrosive agents, and at least four different metals or alloys, are exposed to the corrosive materials. The corrosive agents are hydrogen sulfide and hydrogen chloride; and the metals present are steel, admiralty metal, red brass, and nickel-aluminum bronze.

EXAMPLE 1—RE-RUNNING ACID-TREATED CRACKED DISTILLATE

The first example is of a former operation at our Baltimore, Maryland, refinery wherein a cracked distillate from Pecos crude was treated with sulfuric acid in batch agitators to reduce the sulfur content of the gasoline, with subsequent distillation of the acid-treated distillate. Six to eight pounds of 98-percent sulfuric acid per barrel were required for a final product with a sulfur content of 0.15 percent, and 14 to 16 pounds for a finished product of less than 0.1 percent sulfur.

The re-run still consisted of a pipe-still and bubble-tower system in which the gasoline was flashed-distilled in the tower and the tower bottoms circulated through the furnace for heat. A maximum liquid temperature of 415° F. was maintained in the pipe still, and 30 pounds of steam per barrel was injected into the base of the tower for stripping. The vapor and condenser system was of steel and cast iron.

The amount of sulfur dioxide released for different quantities of acid and for different rates of charge was determined by analyzing the effluent streams (gasoline, water, and gas) for sulfur dioxide. The results are plotted in Figure 1. The individual points are actual determinations from the commercial equipment. A laboratory method (method No. 3 in appendix) was developed which gave the sulfur-dioxide release from a given acid-treated distillate within 2 percent of the actual value obtained on the commercial unit.

Inasmuch as the products of corrosion by sulfur dioxide are water-soluble, the rate of corrosion for a given rate of sulfur-dioxide evolution could be ascertained by determining the iron (method No. 4) content of the condensate water. The actual iron loss in pounds per hour for several rates of sulfur-dioxide evolution is given by curve **A**, Figure 2. From Figure 1, the sulfur-dioxide release for a charging rate of 150 barrels an hour with a 16-pound acid treatment was shown to be 60 pounds an hour—which would give, from Figure 2, an iron loss of 10 pounds an hour, or 240 pounds a day.

From inspection records it was found that the cast-iron condenser sections usually failed, and had to be replaced after having lost about one third of their total weight. The effective loss of iron was, therefore, three

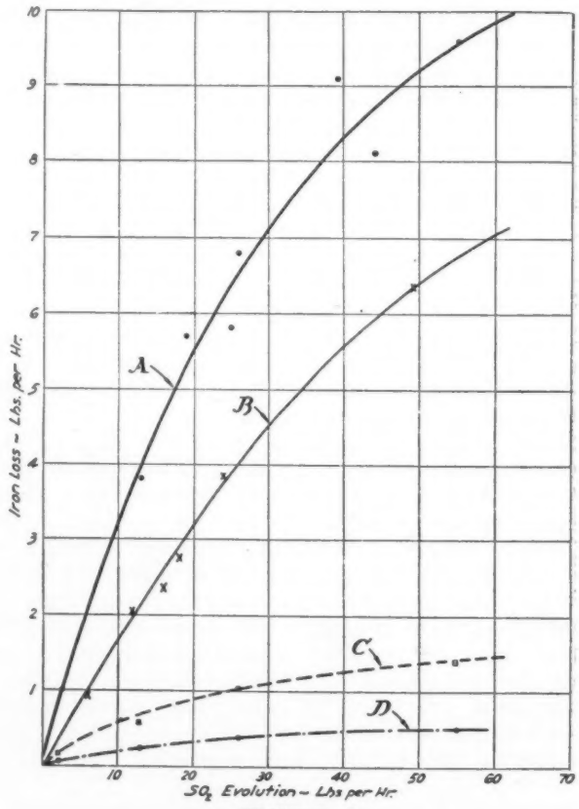


FIGURE 2

times that shown in Figure 2. As the average cost of a pound of a cast-iron condenser section was $0.08, the actual value of a pound or iron loss through corrosion was $0.24. Therefore, the value of metal loss through corrosion in the example given above was $57.60 a day.

The first attempt at chemical protection was the circulation of large volumes of caustic-soda solution through the condenser system. This protected the lower half of the condensers, but did not protect the upper portion. The iron loss each hour with caustic-soda circulation is given by curve **B**, Figure 2.

As a second attempt, gaseous ammonia was injected into the distillation system to neutralize the sulfur dioxide, and the resultant iron loss when using one equivalent $[(NH_4)_2SO_3]$ of ammonia is given by curve **C**, and for two equivalents by curve **D**. The relationship between the ratio of ammonia to sulfur dioxide and the decrease in iron loss is given in Figure 3. It will be seen that twice the theoretical amount of ammonia was required to reduce the iron loss by 95 percent. The routine control procedure was to analyze by method No. 3 each tank of treated distillate for sulfur-dioxide release before charging to the ru-run unit, and the necessary amount of ammonia to obtain the desired protection was calculated. When this distillate was then charged to the still, the ammonia-injection rate was set at the predetermined value. Hourly samples of condensate water were checked by the stillman for iron

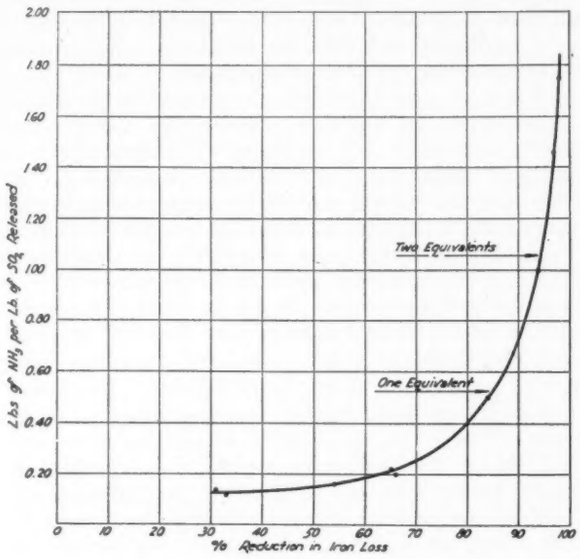


FIGURE 3

content, using method No. 4, and the ammonia readjusted as necessary. The standard comparison colors for iron content were calculated as "pounds of iron loss per day." This figure, being recorded by the stillman hourly, had a very salutary effect on the operators in maintaining a low iron loss.

The final control of corrosion in this system was the equivalent of "removal of source of corrosion before charging." This was accomplished by installing a Stratford continuous treating process[2] which gave a treated product containing a minimum of sulfuric-acid reaction products—which, obviously, decreased to a minimum the sulfur-dioxide evolution on re-distillation. The results were:

	98-Percent Acid Used	
	15 Lb. per Barrel	8 Lb. per Barrel
Sulfur-dioxide evolution, lb. per 1,000 bbl.	38.0	20.0
Iron loss, no ammonia, lb. per 1,000 bbl.	2.0	1.1
Ammonia used, lb. per 1,000 bbl.	20.0	15.0
Iron loss, with ammonia	0.1	0

CORROSION OF CRUDE DISTILLATION EQUIPMENT

The serious corrosion of crude distillation equipment usually occurs from the combined attack of hydrogen chloride and hydrogen sulfide. Other corrosives, such as mercaptans, organic acids, etc., are usually minor in importance, and may be disregarded if the system is properly protected against the attacks of hydrogen chloride and hydrogen sulfide.

Hydrogen sulfide which occurs naturally remains in solution in the crude, and is released on heating. Probably most of the hydrogen sulfide encountered in crude distillation is produced during distillation by the thermal decomposition of sulfur-containing compounds, particularly those of the aliphatic series such as the mercaptans.

Hydrogen chloride may occur as such in the crude oil through acidization of oil wells, but it is generally agreed that the major source is from the hydrolysis of alkaline earth salts during distillation.

Inasmuch as hydrogen chloride and hydrogen sulfide are almost always found together in crude oil, the resultant corrosion of crude distillation equipment is through their combined effect rather than through each individually. It is certain that traces of hydrogen chloride greatly accelerate the rate of corrosion from hydrogen sulfide. This is due to a cyclic reaction within the vapor and condenser system, wherein hydrogen chloride attacks the iron to produce ferrous chloride. The iron of the ferrous chloride is then precipitated as the sulfide by hydrogen sulfide, thus freeing the hydrogen chloride for additional attack on the iron. It is reasonably certain that this cyclic reaction is accelerated by the presence of free oxygen. Accepting this cyclic activity of hydrogen chloride, it is evident that the major problem in preventing corrosion of distillation equipment is the neutralization of the hydrogen chloride.

The substantial reduction or prevention of hydrogen-chloride corrosion may be accomplished in a number of ways, such as by removing the salts from the crude before distillation, by neutralizing the hydrogen chloride after release by alkaline chemicals, by the use of special alloys in equipment fabrication, or by combinations of two or more of these methods.

DE-SALTING CRUDE OIL

Methods are now available[3, 4, 5, 6] for successfully removing all but a trace of the salts originally occurring in a crude. Thus at Continental's Artesia, New Mexico, refinery, the Petreco process is reducing the salt content of the crude charged from about 100 pounds down to 7.7 pounds per 1000 barrels.

De-salting equipment and processes have been extensively discussed in the literature; but the literature on the control of de-salting operations is not extensive, and is far from uniform.

The control of a de-salting operation is usually quite critical. An exact balance of temperature, wash-water quantity, pressure, degree of emulsification and separation (settling time, electrostatic field, filtration, or centrifuging) must be maintained at all times for uniform results. In view of these variables, the correct conditions for optimum separation of salt from any given crude by any specific process must be determined.

A rapid and accurate method for determining the salt content of the crude before and after de-salting is required for process control. The Continental phenolic water-wash method (method No. 1 in appendix) is recommended for routine control work.

The usual procedure in controlling de-salting-plant operations is to determine the salt content of the crude oil before charging it to the process. When stratification in the crude-oil tank is expected, several samples taken from different tank levels should be tested. With these test data available, it is possible to pre-set the con-

ditions at the de-salting plant for the maximum removal of salt.

The effluent crude from the de-salter should be examined as frequently as experience dictates, to determine efficiency and to control satisfactorily the desalter operation. This examination may involve either a test for salt content or a test for hydrogen-chloride release by the distillation method. If experience shows that there is a wide variation in ammonia requirements at the crude distillation stills, probably the latter test is preferable.

PREVENTION OF CORROSION BY THE USE OF ALLOYS

The use of special alloys to overcome corrosion has developed rapidly during the past few years, and extensive discussions on the subject are available in the literature. As a rule, the use of special alloys for corrosion prevention is limited to locations where the corrosion is so severe that the usual chemical protective measures fail.

Special alloys are frequently used to combat a corrosive-water condition. In doing this care must be exercised in selecting a protective chemical for corrosion protection on the oil-vapor side of these tubes, because the alloy for corrosion protection on the water side of the exchanger may be rapidly attacked by the chemical protective agent used in the oil vapor. The discussion of the use of alloys for corrosion protection is limited to this one admonition on the relationships which may exist between alloy and chemical corrosion protection.

CHEMICAL METHODS OF PREVENTING CORROSION

To control the hydrogen-chloride and hydrogen-sulfide corrosion of distillation equipment, the amount of these corrosive agents which will be released during distillation of a given crude must be determined. Fair accuracy is required in this determination, inasmuch as the data from this test will be the basis for determining the amount of neutralizing chemical to be used. The amount of hydrogen chloride and hydrogen sulfide released on distillation of the crude oil may be determined either by analysis of the effluent streams from the distillation equipment for the chloride and sulfide content or by the direct measurement of the hydrogen chloride and hydrogen sulfide which will be released by distillation in our laboratory test method (method No. 2).

The determination of the quantities of corrosives by the analysis of the effluent streams is too complex for control purposes, but is essential for the obtaining of basic data from which accurate control methods may be developed. Laboratory methods, as a rule, do not give the same hydrogen-chloride and hydrogen-sulfide release as a commercial unit. It is, therefore, necessary to obtain correction factors by the detailed analytical determination of corrosives from the commercial equipment for comparison with data from the laboratory method.

There seems to have been little work reported on the formation of hydrogen chloride by the hydrolysis of the alkaline-earth chlorides under conditions similar to those existing in crude distillation. It is known that magnesium chloride is probably the main offender; but there is, for example, a question as to whether calcium chloride produces free hydrogen chloride by hydrolysis in crude-oil distillation.

By using our control method (method No. 2) for the determination of the release of hydrogen chloride from the distillation of crude oil, a general idea may be obtained as to the relationship between hydrogen-chloride release and salt content. An Oklahoma crude was water-washed and filtered until it was free of chlorides. It showed no hydrogen-chloride release by method No. 2. Various quantities of magnesium chloride were added to the crude, and the hydrogen-chloride release on distillation was determined. The results are given in Figure 4. A magnesium-chloride content of 150 pounds per 1000 barrels gave a hydrogen-chloride release of 45 pounds, which is equivalent to 39 percent complete hydrolysis. At lower concentrations, for example, below 5 pounds of magnesium chloride, the results are less reproducible, but indicate complete hydrolysis of the salt. The dotted line indicates the theoretical hydrogen-chloride release for complete hydrolysis. It should be realized that these data are for but one set of conditions, and may be varied widely by the conditions of test.

Sodium chloride and calcium chloride, both alone and in the presence of magnesium chloride, in crude oil were studied to determine whether they would hydrolyze and release hydrogen chloride on distillation. Sodium chloride, either alone or with magnesium chloride, proved to be inert, as was expected. Calcium chloride alone, in concentrations up to 200 pounds per 1000 barrels, showed practically no hydrogen-chloride release—the quantity released being only about ½ pound per 1000 barrels and, therefore, within the error of a blank determination. In the presence of both magnesium chloride and calcium chloride up to 30 pounds per 1000 barrels of calcium chloride, the hydrogen-chloride release was substantially the same as shown in Figure 4 for magnesium chloride alone, the calcium chloride apparently having no effect.

When very large quantities of calcium chloride, i e., 200 pounds per 1000 barrels, were present with magnesium chloride, there seemed to be a suppression of the hydrolysis of the magnesium chloride—less hydrogen chloride being released than for the corresponding amount of magnesium chloride alone. The results were erratic; and, as the salts in high concentrations were added to the crude in solid form, the hydrolysis-suppression data are questioned. It is evident that extensive study of the salt systems in crude oil is needed before a full understanding of the hydrogen-chloride release during crude distillation is obtained.

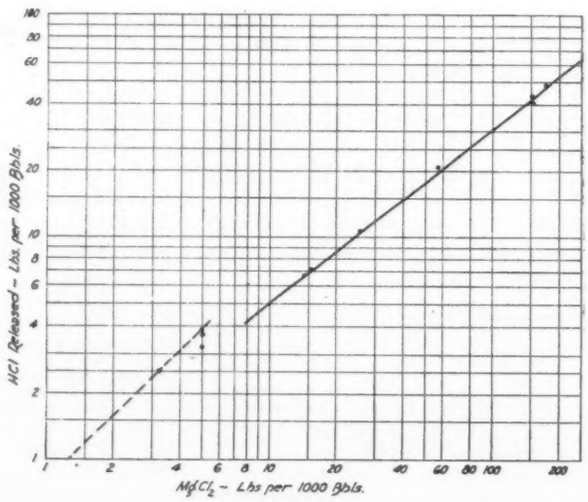


FIGURE 4

It is apparent, however, that the presence of magnesium chloride is highly detrimental, but corrosion prevention may be accomplished either by salt removal, as previously described, or by chemical neutralization, as for example, by ammonia.

THE USE OF AMMONIA TO PREVENT CORROSION

Ammonia has proved to be the most satisfactory neutralizing chemical for hydrogen-chloride and hydrogen-sulfide corrosion, and the trade literature amply covers the mechanics of its use in many successful installations.[1, 7, 8, 9] There is, however, a wide difference of opinion as to the correct amount of ammonia to use. The minimum use reported is that required to neutralize the hydrogen chloride only, while the maximum represents a surplus over the equivalent quantity required for neutralization of both the hydrogen chloride and the hydrogen sulfide.

In an all-iron system, such as that described by Puckett,[7] complete protection of the iron may be obtained by the use of a large excess of ammonia—probably neutralizing to a pH as high as 9.0. In an all-iron system this is certainly the most positive and simplest method of protection, and is economical unless large volumes of ammonia must be used to neutralize excessive amounts of hydrogen sulfide. In such case, however, the quantity of ammonia may be decreased until an economic balance is reached between cost of iron loss vs. cost of ammonia.

In most refineries, however, the crude distillation system includes both iron and copper alloys, such as admiralty metal or red brass. The use of such copper-bearing alloys greatly complicates ammonia control; but, regardless of this, these copper alloys are frequently necessary because of bad water conditions. The brasses as a whole are relatively safe from corrosion under substantially acid conditions, but are rapidly attacked under alkaline conditions[10]—thus making it impossible to add large amounts of ammonia for complete iron protection.

The literature indicates a wide diversity of opinion as to the safe amount of ammonia to be used in a distillation system containing brass. Some report safe use of the brasses in an ammonia-protected system with a pH as high as 8.5, while others report rapid attack with a pH as low as 7.5. The manufacturers of brass tubes usually recommend pH values less than 7.5 for protection of the copper alloys. Most references indicate that a higher pH than 7.5 is required for the protection of iron.

This difference of opinion may arise through a lack of understanding of the relationships between pH and the quantity of corrosive chemicals present, and to the mechanics of ammonium-sulfide attack on brass. Admiralty metal has been found to be relatively free from attack by large volumes of hydrogen sulfide, provided hydrogen chloride is absent or has been neutralized. If, however, sufficient ammonia is used to neutralize the hydrogen sulfide, the brass is rapidly attacked. Preliminary tests indicate that this probably is due to the fact that the ammonium sulfides dissolve or disintegrate the protective copper-sulfide film which is formed on the copper in the simple hydrogen-sulfide-copper system. This reaction is accelerated in the presence of free oxygen.

CONTROL OF AMMONIA BY pH OF STREAMS

For a theoretical study of the pH scale, the reader is referred to such authorities as Taylor.[11] However, a few of the fundamental principles may be reviewed to clarify the subsequent discussion. The pH scale is a measure of the hydrogen-ion concentration or the "acidity" vs. "alkalinity" characteristic of a system. It does not measure the quantity of acid, alkali, or salt present. Water solutions of salts of strong acids and strong bases (which are slightly hydrolyzed) and salts of weak acids and weak bases (extensively hydrolyzed) have a neutral reaction, i. e., a pH of 7. In the case of salts of strong acids and weak bases, the solutions are acidic in character, i. e., they have a low pH value which depends upon the concentration of the salt. Thus a 0.01 N solution of ammonium chloride shows a pH value of 5.6. In like manner, salts of weak acids and strong bases give high pH values.

Figure 5 and 6 have been prepared to show the relationship between pH and the amount of ammonia required to neutralize several systems of hydrogen chloride and hydrogen sulfide. Curves **A, B,** and **C** (Figure 5) represent the actual concentration of chlorides and sulfides found in the condensate from a crude distillation still. Curves **D** and **E** to **F** show the effect of greater quantities of hydrogen chloride and hydrogen sulfide, respectively, than the concentrations reported in curves **A, B,** and **C.** Solutions of hydrogen chloride and hydrogen sulfide of the concentrations given in Table 1 were prepared, and the

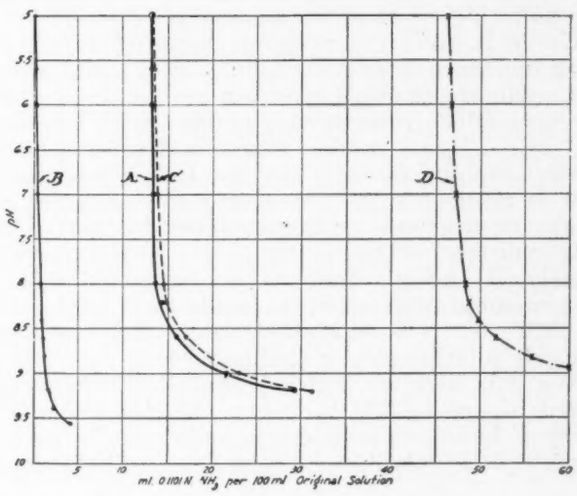


FIGURE 5

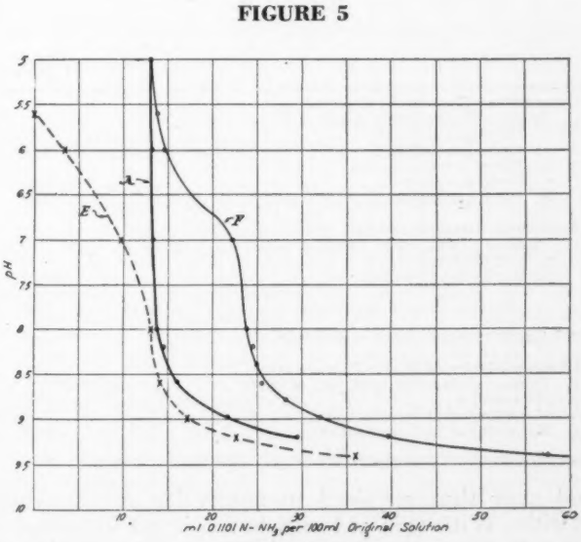


FIGURE 6

number of milliliters of 0.1101 N ammonia required to give a pH range of 5 to 9 was determined, using 100 ml. of original solution. The resulting curves give a measure of the relative amounts of ammonia required to neutralize the hydrogen-chloride-hydrogen-sulfide systems to any desired pH. The pH data diverge slightly from a theoretical buffer solution

TABLE 1

CURVE	A	B	C	D	E	F
Concentration:						
HCl N	0.01464	.....	0.01464	0.051	.....	0.01464
H_2S N	.....	0.00354	0.00354	0.00354	0.0788	0.0788
Ammonia Equivalent:						
Ml. of 0.01101 N:						
Chloride ion, Cl	13.3	.....	13.3	46.3	.....	13.3
Acid sulfide, HS	.....	1.6	1.6	1.6	35.8	35.8
Sulfide, S	.....	3.2	3.2	3.2	71.6	71.6
Total Ammonia (Cl+S):						
To acid sulfide	.....	1.6	14.9	47.9	35.8	49.1
To sulfide	.....	3.2	16.5	49.5	71.6	84.9

because of the increase in volume due to the ammonia solution used.

Curve **A** shows the ammonia required to neutralize the straight hydrogen chloride. From a pH of 5.6, where the equivalent quantity of 13.3 ml. of ammonia solution was required, down to a pH of 8, less than 1 ml. of the ammonia solution was required. At 8.5 only 2.2 ml. more than the equivalent was needed. However, beyond a pH of 8.5 large amounts of ammonia are required to raise the pH a slight amount, showing the buffering effect of the ammonium chloride.

Curve **B** gives the ammonia requirement for the pure hydrogen-sulfide solution. A very rapid rise in pH results from small increments of ammonia, until the acid-sulfide equivalent is reached with 1.6 ml. at 9.1 pH. Thereafter the ammonia requirement increases rapidly, showing that the full sulfide equivalent is reached at 9.5 pH. Curve **C** shows the ammonia requirement for the combined hydrogen-chloride-hydrogen-sulfide system. It follows curve **A** closely. At 8.5 pH the total hydrogen-chloride-hydrogen-sulfide equivalent is reached at 16.5 ml. Curve **D** shows that a more highly concentrated hydrogen-chloride solution gives a similar curve.

We can, therefore, conclude that, in a system composed of appreciable hydrogen chloride but only a trace of hydrogen sulfide, ammonia may be used to reach a pH of 8 to 8.5 with very little surplus ammonia

TABLE 2

	Lbs. per 1,000 Bbl.
A. Quantity of Corrosives Released:	
1. By analysis of effluent streams:	
a. Hydrogen chloride	3.15
b. Hydrogen sulfide	0.36
2. By laboratory distillation:	
a. Hydrogen chloride	4.6
b. Hydrogen sulfide	0.46
B. Ammonia Requirements:	
1. Theoretical equivalent based on (A-1):	
a. For hydrogen chloride	1.47
b. For hydrogen sulfide	0.36
Total	1.83
2. Actual ammonia injected into still	2.00
C. Characteristics of Water Condensate:	
1. Volume, gallons per 1,000 bbl. of crude	708
2. pH value	8.5
3. Normality of hydrogen chloride	0.01464
4. Normality of hydrogen sulfide	0.00354

used over that required to neutralize the hydrogen chloride. With this pH of 8 to 8.5 in an iron-copper-alloy distillation system, there would probably be little or no attack on copper alloys, and the iron would be fully protected.

Figure 6 gives the effect of a higher concentration of hydrogen sulfide with the same hydrogen-chloride concentration shown in Figure 5. Curve **A** is the same straight hydrogen-chloride titration reported in Figure 5, while curve **E** is the titration of the straight hydrogen-sulfide solution (22 times the concentration of that in **B** of Figure 5). Curve **F** is the titration curve for the combined hydrogen-sulfide-hydrogen-chloride system. Here we find a very different condition when comparing the hydrogen-sulfide-hydrogen-chloride solution curve with the straight hydrogen-chloride solution curve. Even at a pH of 5.6, more ammonia is required than the hydrogen-chloride equivalent. With higher pH values the ammonia requirement increases rapidly, until at a pH of 8.5 practically twice as much ammonia has been used as was required for the hydrogen-chloride neutralization. This large excess of ammonia in the form of the acid sulfide would cause rapid attack on the copper alloys. A study of curve **F** shows that, if corrosion of copper alloys by ammonia is to be avoided, the pH should be kept below 6. This pH of 6, however, is definitely too low for iron protection.

In this last system it is impossible to protect both the iron and the copper alloys with ammonia. Under this condition the most logical thing to do is to change to an all-iron system to permit the use of an excess of ammonia. Another expedient which has proved successful with hydrogen chloride and large volumes of hydrogen sulfide is to use a water-jet condenser and so to flood the condensate system with water that the hydrogen chloride and hydrogen sulfide are diluted past the danger point. This last expedient has worked reasonably well at our Artesia, New Mexico, refinery.

EXAMPLE NO. 2

Our No. 5 Foster-Wheeler crude still at Ponca City, Oklahoma, may be used as an example of the use of the ammonia method for the corrosion protection of crude distillation equipment containing both iron and copper alloys. The equipment consists of a 10,000-barrel-per-day single-flash single-tower Foster-Wheeler unit. The operation involves the reduction of Oklahoma City crude to a 40-percent bottom. The flash temperature is 600° F.

The corrosive agents consist of hydrogen chloride with only a small quantity of hydrogen sulfide. The salt content is relatively high—82 pounds per 1000 barrels. Serious trouble from deposition of salt in the heat exchanger system is overcome by maintaining sufficient pressure to prevent the vaporization of the water. No de-salting operation is used.

Table 2 summarizes the data required for the proper control of the corrosion in the system under discussion. The hydrogen-chloride release of 3.15 pounds per 1000 barrels is ample for severe corrosion if not neutralized, but the hydrogen-sulfide production is so low that it is negligible. The concentration of hydrogen chloride and hydrogen sulfide in the water is that given in curve **C**, Figure 5. In view of the low hydrogen-sulfide content, sufficient ammonia is used to give a pH value of 8.5. The ammonia injection, based on hourly pH readings, is controlled to give a resultant pH value of 8 to 8.5 on the effluent water.

From Table 2 it will be seen that the hydrogen-chloride release as determined by the laboratory is higher than that found on the unit. This is at least partly due to the low flash temperature (600° F.) of this particular operation. Rather than vary the laboratory procedure to decrease the hydrogen chloride released, we use the standard procedure and multiply the results by a factor (0.67 in this case) to estimate the probable release on the commercial operation.

RATE OF CORROSION

Due to a rather severe water condition, it is necessary to use copper-bearing alloys in the condensers and coolers. Both steel and admiralty tubes are used in heat exchangers. The maintenance records show the probable average tube life for the various services and metals to be:

1. Vapor to crude exchangers:
   a. Admiralty metal—practically indefinite life—more than 5 years.
   b. Steel, on heavier streams—10 to 20 months.
2. Condensers and coolers:
   a. Admiralty metal—12 months—all failures due to dezincification from water side. No failures from vapor side.
   b. Red brass—no failures after 18 months.
   c. Nickel-aluminum bronze—one tube failure in 30 months of service.

Formerly, admiralty metal was used in all condensers and coolers; but, due to the short life caused by dezincification from the water side, all replacements during the last 18 months have been with red brass. The long life of admiralty in exchangers indicates that this copper alloy is safe with a pH of 8.5 maximum with the reported concentrations of chlorides and sulfides.

Although we have not had failures of the red brass, there are indications that a slow attack from the vapor side is taking place. The condensate carries a trace of copper. On another unit, under similar conditions, we have had a few failures of red brass from the vapor side. The estimated life obtained by extrapolation on probability paper[12] is from 42 to 60 months.

It, therefore, appears that under these conditions a pH of 8.5 is too high for red brass, but a lower pH causes an increased attack on steel. We have not as yet determined the relative economy of a lower pH.

The experimental bundle of nickel-aluminum bronze is showing excellent results, and may be a solution to this particular problem.

Although a pH of 8.5 appears safe for admiralty and fairly safe for red brass on this installation, it should be remembered that this is true only because of the low hydrogen-sulfide release. At other plants with more hydrogen sulfide, we have observed very rapid loss from red brass with pH's of 7.5 to 8.0. It, therefore, appears that the question of ammonia control by pH must be determined for every individual unit and for each particular crude.

APPENDIX

METHODS OF TEST

METHOD NO. 1—TO DETERMINE THE HALOGEN SALT CONTENT OF CRUDE OIL AS SODIUM CHLORIDE

Apparatus

a. 1000-ml. separatory funnel.
b. 100- and 250-ml. graduated cylinders.
c. 250-ml. Erlenmeyer flask.
d. Burette, filter paper, funnels, hot plate, etc.

Solutions

a. Phenol solution: 88-percent USP phenol in 12 percent water, must be clear and colorless; keep in brown bottle.
b. Benzene or toluene, technical grade.
c. Standard 0.04881 N silver nitrate ($AgNO_3$) (8.293 g. $AgNO_3$ per liter. 1 ml. = 20 lb. sodium chloride per 1000 bbl.)
d. Cadmium nitrate ($Cd(NO_3)_2$—10-percent solution in water.
e. Potassium chromate (K_2CrO_4)—5-percent solution as indicator.
f. Sodium-hydroxide solution, ½ percent.
g. BDH* Universal indicator.

Procedure

a. Transfer exactly 125 ml. of the oil sample under test (after thorough agitation) into the separatory funnel.

b. If the oil is very viscous, add 125 ml. benzene or toluene. Thoroughly agitate to mix the oil and benzene. With most crude oils lighter than 34 API gravity, the solvent is unnecessary.

c. Add 200 ml. of boiling distilled water, and shake gently for 3 min. Frequently relieve pressure by opening the stop cock of the inverted funnel. Add 20 ml. of phenol and 30 ml. of boiling distilled water, and shake for 5 min.

d. Allow the mixture to stand until more than 100 ml. of clear-water solution has separated. Filter off exactly 100 ml. of the water into a graduated cylinder through two sheets of heavy qualitative filter paper.

e. If negligible quantities of sulfide and mercaptans are present, transfer the 100 ml. of filtered solution to an Erlenmeyer flask; adjust to 6.5 pH, and add 2 ml. of the chromate indicator. Titrate the cold (not over 85° F.) solution with 0.04881 N $AgNO_3$ to a light orange end point, using a blank of water and chromate for color comparison.

f. If either sulfides or mercaptans or both are present, they must be removed before the chlorides can be determined. The 100 ml. of solution from (d) is transferred to a 250-ml. beaker, 1 ml. Universal indicator added, and the solution adjusted to a pH of 6.5-7.0 (light greenish yellow). The sulfides and mercaptans are precipitated with a slight excess of $Cd(NO_3)_2$. Allow to stand 30 min. and transfer to centrifuge tube. Centrifuge until the solution is clear and the precipitate is a dense, firm mass. Decant the clear solution to the Erlenmeyer flask, filtering if necessary. Rinse the beaker with 10 ml. distilled water into the centrifuge tube. Thoroughly wash the precipitate by shaking, and re-centrifuge. Decant the clear wash water into the solution in the Erlenmeyer flask, and adjust to exactly 6.5 pH (yellow). Titrate for chlorides as in (e).

Calculation

(ml. $AgNO_3$ — ml. blank) × 20 = lb. NaCl per 1000 bbl.

This relationship is true only if the exact volumes and concentrations are used. If the determination is desired in other units, the $AgNO_3$ solution may be adjusted accordingly. [Thus, ml. of 0.05379 N $AgNO_3$ (9.138 g. per liter) = 10 g. NaCl per barrel.]

Discussion

a. The use of phenol and the aliquot portion of solution results in a rapid determination suitable for control purposes. The phenol not only gives rapid separation of the water layer, but also promotes the extraction of asphalt or wax-protected salt crystals from the crude. A similar method has been suggested by Blair[14] in which a special "de-stabilizer" is used in place of phenol. The use of the first 100 ml. of solution as an aliquot part has been justified experimentally by separating all of the wash water and analyzing successive portions for chloride content. If the crude oil contains appreciable free water, the aliquot portion should be corrected.

b. In the case of most "sweet" crudes the cadmium separation is unnecessary. If, however, a dark precipitate appears when starting the silver-nitrate titration, the presence of sulfides is indicated. In the case of unknown crudes, a second small aliquot portion of water from the separatory funnel may be checked with $Cd(NO_3)_2$ solution before proceeding with the determination.

c. The success of the cadmium removal of the sulfides and mercaptans depends on the exact adjustment of the pH values. In solutions with a pH value slightly lower than 6.5, the precipitation of the mercaptans is not complete, and some chloride may be carried down with the sulfide.

d. The BDH Universal indicator is recommended, as it permits the adjustment to both 6.5-7.0 and to 6.5 pH. At the latter value it is a clear yellow, which does not interfere with the chromate indicator. If, after the addition of the

* British Drug House, Ltd.

indicator, the color is not a bright yellow, the solution can be adjusted to 6.5 pH by comparing the color with a blank of water and chromate.

METHOD NO. 2—TO DETERMINE HYDROGEN CHLORIDE AND HYDROGEN SULFIDE RELEASED FROM CRUDE-OIL DISTILLATION

Apparatus

The apparatus consisting of an interchangeable ground-glass joint assembly for steam distillation is shown in Figure 7, and includes:

a. Long-neck 1000-ml. flask with thermometer well.
b. Thermometer well and high range ASTM distillation thermometer (D 86-35).
c. Adapter neck and steam-delivery tube and source of steam.
d. 18-in. jacketed water-cooled condenser.
e. Special adapter.
f. 500-ml. Erlenmeyer flask receiver.
g. ASTM absorber (D 90-34T).

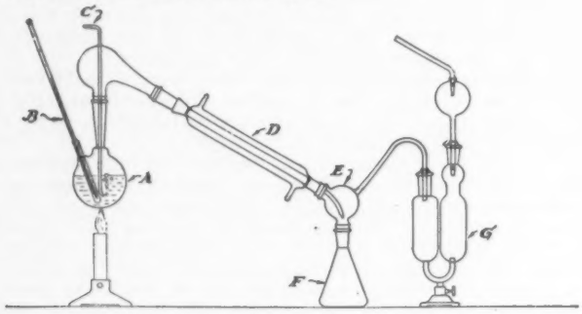


FIGURE 7

Solutions

a. Sodium carbonate, 3.306 g. Na_2CO_3 per liter.
b. Standard hydrochloric acid, 0.08623 N.
c. Hydrochloric acid, 0.2 N.
d. Hydrochloric acid, 4.0 N.
e. Potassium hydroxide, 5 percent KOH.
f. Cadmium nitrate, 10-percent $Cd(NO_3)_2$.
g. Standard silver nitrate, 7.328 g. $AgNO_3$ per liter.
h. Standard iodine solution, 0.09227 N I_2.
i. BDH Universal indicator.
j. Potassium-chromate indicator, 5 percent K_2CrO_4.

Procedure

A. *For hydrogen chloride only:*

a. Deliver 500 ml. of crude oil to be tested into the flask (**A**) and assemble equipment.

b. The Erlenmeyer flask receiver (**F**) is empty, but the absorber (**G**) should contain exactly 45 ml. Na_2CO_3 solution (3.306 g. per liter).

c. Heat is applied, and the temperature raised to 250° F. in 10 min.

d. Steam is introduced into the flask, and so regulated that approximately 40 ml. of water condensate will form throughout the distillation.

e. The temperature is raised at such a rate that 500° F. will be reached in 30 min. and 650° F. in an additional 15 min. (total time from starting of heating, 55 min.).

f. Upon reaching 650° F. the heating and steam injection is immediately stopped.

g. The condensate in the receiver is transferred to a separatory funnel and, after shaking, the water layer is drawn from the distillate into the absorber (**G**). Two 15-ml. distilled water washes are used to rinse the receiver (**F**) and to wash the gasoline in the separatory funnel. During shaking, the funnel should be kept stoppered except for occasional ventings to relieve pressure. Transfer the wash water to the absorber.

h. Make the total volume in the absorber up to about 150 ml. and back titrate with standard hydrochloric acid (0.08623N) using methyl orange as an indicator. Make a blank titration of the hydrochloric acid against 45.00 ml. of the sodium-carbonate solution.

Calculation:

(ml. HCl for blank — ml. HCl for titre) = g. HCl per barrel of oil.

or

(ml. HCl for blank — ml. HCl for titre) × 2.2 = lb. HCl per 1000 bbl.

B. *For both hydrogen chloride and hydrogen sulfide:*

a. Place 50 ml. of 5-percent potassium hydroxide in both the receiver (**F**) and the absorber (**G**).

b. Proceed with the distillation as in (A).

c. Transfer the solution from the absorber (**G**) into a 400-ml. beaker, and rinse the absorber with two 15-ml. washes of distilled water.

d. Transfer the contents of the receiver (**F**) to a separatory funnel, shake thoroughly, settle, and draw the solution into the same beaker (**C**). Rinse the receiver and the gasoline with two 15-ml. washes of distilled water, and transfer the wash water to the beaker.

e. Carefully neutralize the solution to a pH of 6.5-7.0 with dilute nitric acid; then precipitate the sulfide and mercaptans with a small excess of cadmium-nitrate solution. Let stand 30 to 60 min. as a filtering aid. Filter through quantitative filter paper. Wash sparingly with cold distilled water, adding the wash water to the filtrate.

f. Readjust the filtrate to a pH of 6.5, add 2 ml. of chromate indicator, and titrate with silver nitrate.

Calculation:

(ml. $AgNO_3$ — ml. blank) × 1.1 = lb. HCl per 1000 bbl. of crude oil.

g. The cadmium sulfide and mercaptides are separated by washing the precipitate on the filter paper with a small volume of 0.2 N hydrochloric acid, which decomposes and dissolves the mercaptides. The volume of acid required depends upon the quantity of mercaptans present, and should be determined by experience for any given crude. The precipitate is washed repeatedly by returning the acid filtrate to the precipitate, which should be stirred while washing, to obtain complete removal of the mercaptides. Finally, sparingly wash the precipitate with distilled water, and discard the washings.

h. The remaining precipitate consisting of cadmium sulfide is transferred with the filter paper to a beaker; add 100 ml. distilled water; disperse the precipitate in the water by thorough stirring. Add 20 ml. of 4 N hydrochloric acid (to make the total solution 0.6 N CHl) and titrate the liberated hydrogen sulfide with standard iodine solution, using starch as an indicator.

Calculation:

(Total ml. I_2 — ml. blank) × 1.1 = lb. H_2S per 1000 bbl.

Discussion

a. For routine control work, where only the hydrogen-chloride release is required, procedure (A) is rapid and more reproducible than the more complex methods requiring the separation of hydrogen sulfide and mercaptans. The latter do not interfere with the titration of hydrogen chloride to a methyl-orange end point.

b. Hydrogen sulfide and mercaptans interfere with all the usual chloride determinations using silver or mercury. If the quantity of hydrogen sulfide is desired, the cadmium separation will be satisfactory if care is taken to have the solution acidities exactly as specified. When very large volumes of hydrogen sulfide and mercaptans are present and the hydrogen-chloride content low, the cadmium precipitate will sweep down some chloride—thus lowering the quantity of hydrogen chloride found. In such cases a check distillation by procedure (A) may be made for the true hydrogen-chloride release.

It is also possible to separate the chlorides from the sulfide and mercaptans by taking an aliquot portion of the original solution (B-d) for each determination. One part is used to determine hydrogen sulfide by the cadmium method. The second portion is neutralized, and an excess of silver-nitrate solution added to precipitate the chlorides (about 10 ml. more than needed for the hydrogen chloride). Add concentrated nitric acid to increase the volume by one third, and boil to decompose all sulfide and mercaptides. Cool and back titrate with standard ammonium-thiocyanate solution, using ferric alum as an indicator according to the standard Volhard procedure.

METHOD NO. 3—FOR DETERMINATION OF SULFUR-DIOXIDE RELEASE FROM ACID-TREATED DISTILLATES

Apparatus

Similar to that in Figure 7, except that a 500-ml. graduated cylinder is used in place of the receiver (**F**).

Procedure

Caustic-soda solution is used in both the receiver and absorber; 500 ml. of distillate is charged to the flask, and

heated to above the boiling point of water. Steam is cut in at a rate equal to the steam ratio to distillate used in the plant (30 pounds per barrel).

The temperature is gradually raised to the maximum temperature reached in the commercial unit (415° F.). Distillation is continued until the predetermined yield of gasoline or distillate has been received in the graduate.

Standard Buffer Solutions of Clark and Lubs[13]

(50 ml. A plus x ml. B diluted to 200 ml.)

A=0.2 M KH o-phthalate B=0.2 M NaOH		A=0.2 M KH_2PO_4 B=0.2 M NaOH		A=0.2 M H_3BO_3* Plus 0.2 M KCl B=0.2 M NaOH	
pH	ml. B	pH	ml. B	pH	ml. B
4.0	0.40	5.8	3.72	7.8	2.61
4.2	3.70	6.0	5.70	8.0	3.97
4.4	7.50	6.2	8.60	8.2	5.90
4.6	12.15	6.4	12.60	8.4	8.50
4.8	17.70	6.6	17.80	8.6	12.00
5.0	23.85	6.8	23.65	8.8	16.30
5.2	29.95	7.0	29.93	9.0	21.30
5.4	35.45	7.2	35.00	9.2	26.70
5.6	39.85	7.4	39.50	9.4	32.00
5.8	43.00	7.6	42.80	9.6	36.85
6.0	45.45	7.8	45.20	9.8	40.80
6.2	47.00	8.0	46.80	10.0	43.90

* Molecular weight of boron, 11.0.

The receiver is thoroughly shaken, and the caustic solution transferred to the absorber. The solution is neutralized, and the sulfur-dioxide content determined iodimetrically.

The distillation conditions may be varied to match any given commercial operation. In actual practice the laboratory has been found to check the sulfur-dioxide release in the commercial equipment within 2 percent.

METHOD NO. 4—TO DETERMINE THE IRON CONTENT OF DISTILLATE

Apparatus

a. 250-ml. Erlenmeyer flask.
b. 100-ml. graduate.
c. 1-ml. dropper.

Solutions

a. 30-percent solution of concentrated hydrochloric acid.
b. Ferroferricyanide indicator:
   10 g. potassium ferrocyanide in one liter of distilled water.
   10 g. potassium ferricyanide in one liter of distilled water.
c. Standard iron solutions of such concentration to cover probable range of iron to be found.

Procedure

To a sample of 90 ml. of the water condensate is added 10 ml. of 30-percent hydrochloric acid and 1 ml. of indicator.

The resultant color is compared with the standard iron solutions to determine iron content.

Discussion

For routine control it has been found desirable to test the condensate hourly. The iron standards may be in any desired units, but the use of "pounds iron loss per 24 hours" has proved very successful.

* See tabulation.

METHOD NO. 5—pH OF CONDENSATE

Although any form of electrometric or indicator method may be used for the routine determination of pH, and although we use the electrometric methods in the laboratory, we have found them too delicate and complicated for the average still operator. The use of a mixed or "Universal" indicator has proved very successful and, if used by comparing with standard buffer solutions, is accurate to 0.2 pH.

We use and recommend the BDH Universal indicator put out by the British Drug House, Ltd., and distributed by Eimer and Amend. The color reactions are:

pH	pH
up to 4.0 red	8.0 green
4.0 deep red	8.5 bluish green
5.0 orange red	9.0 greenish blue
5.5 orange	9.5 blue
6.0 orange yellow	10.0 violet
6.5 yellow	10.5 reddish violet
7.0-7.5 greenish yellow	11.0 deeper violet

0.1 ml. of indicator is used per 10 ml. of solution.

For accurate pH determinations, particularly in artificial light, the color of the unknown solution should be compared with standard buffer solutions containing the same concentration of indicator. Clark and Lubs'[13]* buffer solutions have proved stable and accurate to 0.02 pH against a Beckman glass electrode instrument.

In routine control the stillman is furnished with the indicator and a 10-ml. calibrated test tube in which the condensate is checked hourly. Two standard buffer solutions, representing the minimum and maximum permissible pH values, are furnished in similar tubes. If the pH is outside the given range, the operator can tell by the color whether the pH is higher or lower than the range. The buffer colors should be checked weekly.

BIBLIOGRAPHY

[1] Walter Miller, "Refining Panhandle Crude," *Proc. API* 7, 309 (1926).
[2] M. B. Cooke and A. W. Hayford, "Distillate Treating," *Refiner Natural Gasoline Mfr.* **13** [3] 83; and **13** [4] 125 (1934).
[3] Gustav Egloff, E. F. Nelson, C. D. Maxutov, Charles Wirth, III, "De-salting Crude Oils," *U O P Booklet No. 216;* also *Oil Gas J.* **36** [23] 66 (1937).
[4] J. J. Allinson, "Electric Dehydrating and De-salting," *Proc. API* **18M** [III] 30 (1937).
[5] J. C. Albright, "De-salted Crude Reduces Corrosion," *Natl. Petroleum News* **29** [1] 61 (1937).
[6] D. R. Jones, "Salt Removal from Crude Oil," *Refiner Natural Gasoline Mfr.* **16** [5] 208 (1937).
[7] Robert E. Puckett, "Practical Methods Used to Prevent Corrosion from Mid Continent Crudes," *Oil Gas J.* **36** [19] 44 (1937).
[8] E. R. Woodward, "Anhydrous Ammonia Used in Refining as a Refrigerant, Neutralizer, and for the Retarding of Corrosion," *Oil Gas J.* **33** [17] 33 (1934).
[9] S. S. Shaffer and J. E. Pollock, "Corrosion in Non-pressure Refining Equipment," *Proc. API* **13** [III] 63 (1932). "Metal Losses in Condensers and Tried Methods for Combating Corrosion," *Oil Gas J.* **30** [46] 78 (1932).
[10] Sidney Born and W. L. Nelson, "Corrosive Agents on Admiralty Metal," *Natl. Petroleum News* **25** [29] 27 (1933).
[11] Hugh S. Taylor, *Treatise on Physical Chemistry*, Vol. 2, 901, D. Van Nostrand Co., Inc., New York.
[12] J. S. Walton, "Statistical Treatment of Refinery Problems," *Refiner Natural Gasoline Mfr.* **16** [1] 36 (1937).
[13] *International Critical Tables*, Vol. 1, 82.
[14] Charles M. Blair, Jr., "Determination of Organic Salts in Crude Oils," *Ind. Eng. Chem., Anal. Edn.* **10** [4] 207 (1938).

Identification and Properties of Straight-run and Cracked Residua

A. H. BATCHELDER and H. B. WELLMAN

Standard Oil Company of California, San Francisco

ESSENTIAL differences in the composition and behavior of cracked and straight-run tars and asphalts made advisable the development of a quantitative analytical procedure for their determination. The conventional tests and inspections are unsatisfactory for this purpose. Spot tests, which have been used to determine the presence of cracked residua in fuels and asphalts, are necessarily qualitative, usually hyper-sensitive, and frequently misleading because of the presence in some crudes of traces of asphaltenes insoluble in mineral spirits.

A method which enables clear-cut differentiation of straight-run and cracked asphaltenes is described. Theoretical aspects of fuel-oil blending, with particular reference to the influence of straight-run residua upon the heater-coating indices of cracked fuels, are discussed and illustrated.

This paper was presented at Eighth Mid-Year Meeting, American Petroleum Institute, Lassen Hotel, Wichita Kansas, May 24, 1938.

WHILE cracked tars may be in themselves essentially as stable as straight-run residua, their compatibility with cutters and thinners is usually markedly lower. The lower tolerance of cracked residua is due to their content of condensation products and heavy asphaltenes more easily precipitated by light naphtha than are the asphaltenes found in crude oils or straight-run residua. The poorer solubility of these heavy components is in some measure compensated for by the higher solvency of the naphtha-soluble portion of cracked as compared to virgin tars from the same crude.

Wide differences in the physical and chemical properties of the two types of residua, and the products made therefrom, have made desirable the development of quantitative methods of identification. Also, the use of cracked tars in blended fuels has made necessary consideration of the more important factors which govern sedimentation and heater-coating indices.[1]

COMPATABILITY WITH CUTTERS

It is to be expected that the over-all solvent or protective power of a crude oil would be the limiting factor governing the amount and character of the heaviest asphaltic constituents. Unsolvated or suspended asphaltenes would be either precipitated or filtered out in the passage through the producing formation. Precipitation and filtration might be expected to occur when light and heavy crudes are mixed on the way to the bottom hole. Much the same considerations would govern the extent of the leaching out of any solid asphaltic material in oil sands. Thus asphalts from relatively paraffinic and mixed-base crudes contain little heavy asphaltenes, even though the total asphalt content may be high. The proportion of heavy asphaltenes is, as might be expected, usually high in the more naphthenic crudes, especially those low in gasoline content. The presence in certain California producing sands of asphaltic material less easily dissolved than the heaviest asphaltenes in the crude, but which may be removed by stronger solvents, is evidence for this view.

The occurrence in some heavy crudes of a fraction of a percent of asphaltenes similar in solubility to those found in grahamite, results in positive Oliensis spot tests on straight residual stocks.

Removal from crude of light hydrocarbons, which are precipitants, enhances the inherent stability of the asphaltic constituents, and ordinarily more than compensates for slight skin cracking and the tendency of the heavier asphaltenes to agglomerate or condense on heating.

SPOT AND SOLVENT TESTS

In general, straight residual stocks, irrespective of origin, can be blended in all proportions with each other, and are safely compatible with even the most paraffinic cutter stocks. That stable[1] cracked tars differ from virgin stocks in this respect, only in degree, is illustrated by the photomicrographs of Figure 1, which were taken in a set-up identical with that used by the Naval Boiler Laboratory. It will be observed that both undiluted stocks therein depicted contain what might be termed a trace of suspended or unsolvated particles. Neither stock yielded a perceptible spot when suitably cut back with a solvent which did not cause further separation. Definitely positive spot tests were obtained at the point at which separation of asphaltenes became perceptible. Under the conditions employed in the Oliensis test,[2] the straight-run residuum showed no spot, while a positive result was obtained in the case of the cracked tar.

The Oliensis test enables the **qualitative** detection of traces of asphaltenes or carbonaceous material precipitated under controlled conditions by specified thinners. The formation of a disperse phase, as determined from the spot test, is stated to be indicative of the "heterogeneity" of the asphalt or fuel. It

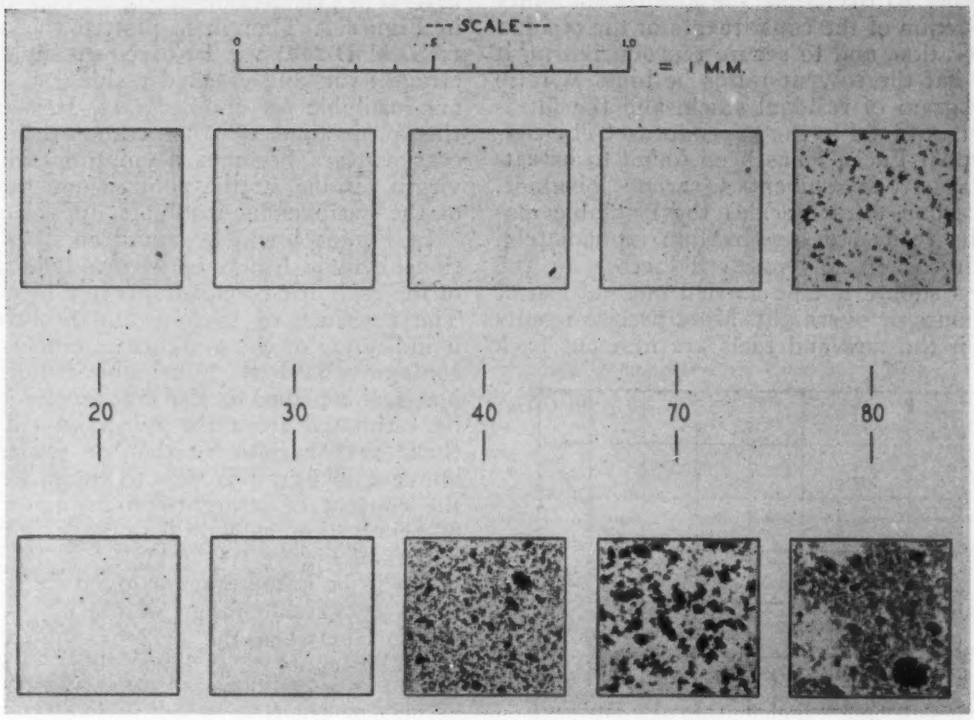


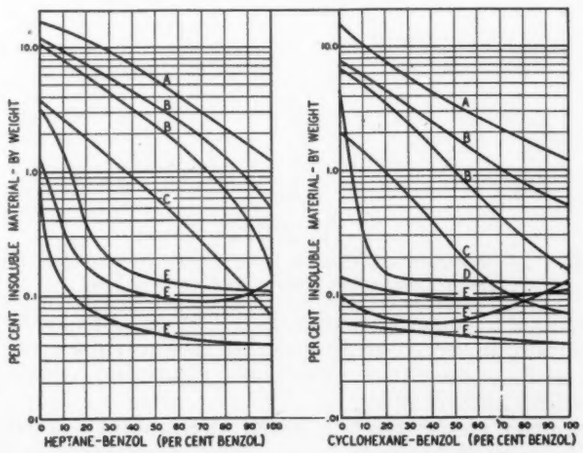
FIGURE 1
Photomicrographs of Cut-back Residua

is felt that Figure 2 is evidence that positive spot tests may be due solely to incompatibility with a particular cutter. In this connection, the following considerations are offered:

1. The fact that the addition of a preponderant number of diluent molecules obscures any mutual solvent or protective action of the oils, resins, and asphaltic constituents must be taken into consideration in the evaluation of any solvent test. The presence of a disperse phase in a cut-back residuum does not necessarily connote a similar condition in the undiluted stock. This applies equally well when the diluent has much the same solvent power (judged by analine point, viscosity-gravity constant, or the like) as the oil content of the tar or asphalt, or is a cut derived from the same crude, inasmuch as the compatibility tolerance may be exceeded.
2. Spot tests are particularly disadvantageous in that even traces of material, which may or may not have been solvated in the undiluted stock, yield positive results. In the case of traces of heavy asphaltic or even carbonaceous material, the state in which they are to be found in the tar or asphalt, and even their presence in a qualitative sense, are of no practical significance.
3. In the usual spot-testing procedure the low solvent ratio results in poor reproducibility in borderline cases. Lowering of the sensitivity by increasing the solvent power of the standard cutter results in amelioration in some instances. A substantial change in solvency brings with it the possibility that negative results will be obtained with stocks the test is intended to reject.

CLASSIFICATION OF ASPHALTIC CONSTITUENTS

Despite the above-mentioned limitations, solvent tests may be used quantitatively to classify the types of asphaltic materials in straight-run and cracked



A—severely-cracked residuum.
B—cracked residuum.
C—cracked gas-oil tar.
D—air-blown asphalt, 22 penetration; 169-deg.-F. melting point.
E—straight residual fuel.

FIGURE 2
Solubilities of Cracked and Straight-run Residua

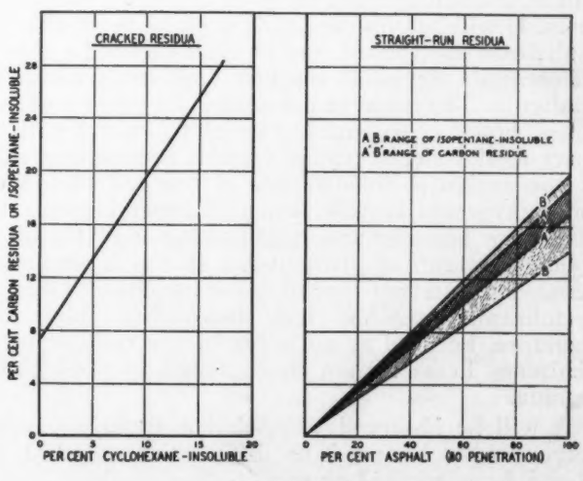

CRACKED RESIDUA
STRAIGHT-RUN RESIDUA
PER CENT CARBON RESIDUA OR ISOPENTANE-INSOLUBLE
A B RANGE OF ISOPENTANE-INSOLUBLE
A' B' RANGE OF CARBON RESIDUE
PER CENT CYCLOHEXANE-INSOLUBLE
PER CENT ASPHALT (80 PENETRATION)

FIGURE 3
Effect of Cracking on Carbon Residue and Solubility of Asphaltenes

residua. In order to overcome the mutual solubility or protective action of the constituents of the residua under consideration, and to secure reproducibility, it is necessary that the solvent ratios be high. A ratio of 20 ml. per gram of residual stock, and the filtration procedure outlined in the appendix to "The Stability of Residual Fuels,"[1] has been found to be satisfactory. For strong solvents (carbon bisulfide, chloroform, carbon tetrachloride) the insoluble materials may be recovered by filtration immediately. In using hydrocarbon solvents, ethyl ether, or the like, filtrations should not be carried out until after standing 10 hours or overnight. More precise results are obtained if the tars and fuels are first cut back

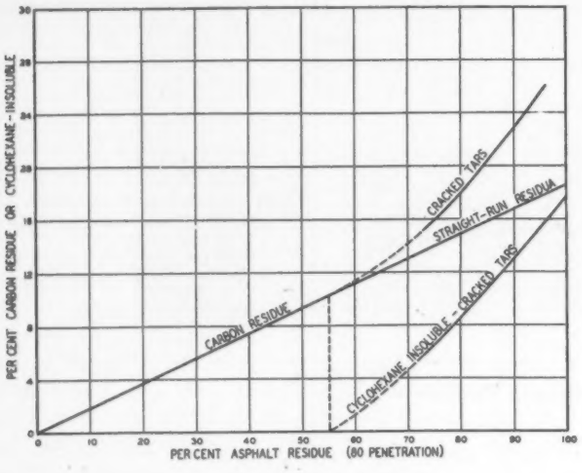


FIGURE 4
Relation of Asphalt and Carbon Residues to Solvent Tests

with as small a quantity of solvent (1 volume, for instance) as to result in a fluid mix, using reflux or a small bomb if necessary. The required amount of solvent may then be readily mixed with the cut-back stocks. In the case of asphalts or heavy tars, it is frequently desirable to cut back with approximately an equal volume of straight-run gas-oil cutter. In most cases the effect of gas oil with its relatively high molecular weight can safely be neglected.

In Figure 2 will be found the results of attempts to classify asphaltic constituents in straight-run and cracked California residua on the basis of their content of asphaltenes insoluble in heptane-benzol mixtures. It will be observed that heptane is an effective asphaltene precipitant, and as such cannot be used to differentiate between cracked and straight-run asphaltenes. The mixture containing 30 percent of benzol is, however, essentially equal to benzol with respect to the virgin residua; yet it precipitates some of the asphaltic constituents of cracked tars. Even more favorable in this respect is cyclohexane. The difference between the cyclohexane- and benzol-insoluble contents of straight-run stocks is essentially zero. The percent cyclohexane-insoluble (that is, cyclohexane-insoluble less benzol-insoluble) can, therefore, be used as an index of the content of asphaltenes heavier than those found in straight-run residua.

It will be observed, also, that a slightly stronger solvent may be used to differentiate normal air-blown from cracked or straight-run stocks.

An interesting correlation, which corroborates the contention that cracking is accompanied by the formation of cyclohexane-insoluble asphaltenes, is found in Figure 3. Therein is plotted the asphalt residue (ASTM D-243) vs. the carbon residue for California straight-run and cracked residua, and the cyclohexane-insoluble for cracked tars. It is significant that the projection of the carbon-residue curve for cracked tars becomes asymptotic with that of the virgin residua, at the point where the extrapolation of the cyclohexane-insoluble line reaches zero.

In Figure 4 will be found an illustration of relationships which may be used to determine the origin of the asphaltic constitutents in a blended tar or fuel. The presence of cyclohexane-insoluble asphaltenes is indicative of the presence of cracked tar. The percentage of *iso*pentane-insoluble material, or the carbon residue, due to the cracked-tar component can be estimated from the left-hand curve. Assuming, then, that carbon residue or *iso*pentane-insoluble above this figure is due to uncracked asphaltenes, the content of straight-run residuum, expressed as 80-penetration asphalt, can be estimated from the curves of Figure 4 (right).

It will be found that for given charging stocks and for a reasonable range of cracking conditions, the relation between the cyclohexane- and *iso*pentane-insoluble contents is linear. The same is true also for the cyclohexane- and ethyl-ether-insolubles, which are nearly equal for most cracked tars.

Further information as to the form in which cutters or residual components were added may be obtained by analysis and comparison of characterization data on overhead stocks.

BLENDING RELATIONSHIPS

Stable cracked residual fuels with satisfactory heater-coating indices are in almost all cases mutually compatible. Ordinarily the log of the heater-coating index is the weighted average of the logs of

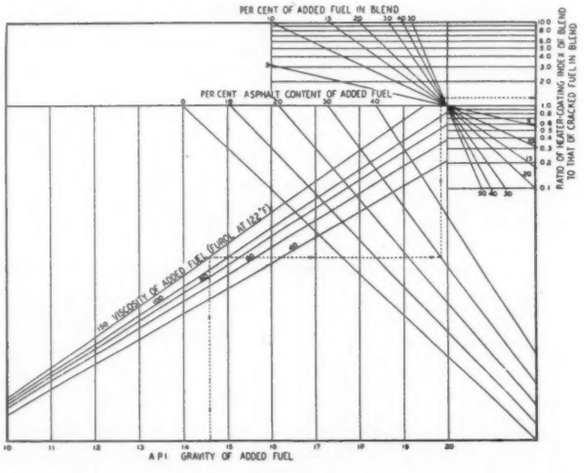

PER CENT OF ADDED FUEL IN BLEND
PER CENT ASPHALT CONTENT OF ADDED FUEL
RATIO OF HEATER-COATING INDEX OF BLEND TO THAT OF CRACKED FUEL IN BLEND
VISCOSITY OF ADDED FUEL (TARS) AT 122°F
API GRAVITY OF ADDED FUEL

FIGURE 5
Effect of Addition of Cut-back or Straight Residual Fuels from California Crude to Cracked Fuel

the heater-coating indices of the component fuels, so that the heater-coating index of a blend may be expected to be equal to or less than the calculated arithmetic average.

Cutter stocks tend to lower the stability of residual tars, the effect being most pronounced with cracked tars, but usually of little moment in the case of virgin residua. Addition of straight-run asphalts to cracked fuels greatly increase their stability, the

(*Continued on Page 312*)

The Catalytic Hydrogenation *of* Octenes to Octanes

A Contribution by the Combined Staffs of Shell Development Company and Shell Chemical Company, San Francisco, California.

A CATALYTIC hydrogenation process has been developed by the Shell Companies which is simple, economical, and particularly adapted to the hydrogenation of octenes produced by polymerization of butylenes. The process operates at low pressure (below 4 atmospheres, gage) and at a temperature not exceeding 200° C. [392° F.].

The process effects substantially complete hydrogenation, and produces thereby high-octane fuels low in acid-heat number and ideally suited for the manufacture of high-octane aviation gasoline.

This paper was presented at Eighth Mid-Year Meeting, American Petroleum Institute, Lassen Hotel, Wichita, Kansas, May 24, 1938.

THE benefits to be derived from the use of high-octane fuels in airplane engines, particularly in those of recent design which operate most efficiently with fuel of a knock rating of 100 on the *iso*octane-heptane scale, are quite pronounced. Whether they find expression mainly in improved fuel economy, in greater load-carrying capacity, greater speed, longer cruising range, or any combination of these and other advantages, the increased value of such fuels as compared with recent standards, is very much in evidence.[1] 100-octane fuel might perhaps be prepared by the addition of large quantities of tetraethyl lead to selected straight-run gasolines; but lead in such proportions would far exceed the present specifications laid down by engine manufacturers, and would lead to objectionable corrosive effects and deposits in the engines. Oxygen-containing compounds can be manufactured which supply an octane-number increase and thereby decrease lead usage; but these compounds are at a disadvantage, compared with hydrocarbons, because of both their lower calorific value per unit of weight and their greater miscibility with water—the latter causing well-known practical difficulties. A more satisfactory fuel is one containing high-octane hydrocarbons, such as *iso*octane. The search for a satisfactory gasoline of high anti-knock value, containing an optimum amount of lead and having a high calorific value, has been carried on intensively, and has led to the development by the Shell Companies of a practical commercial process for the production of octanes of 98-100 octane number, by direct hydrogenation of an octene mixture prepared by butylene polymerization.

A method for the production of the octene mixture has been described by McAllister.[2] The hydrogenation process developed is particularly applicable to the conversion of this octene mixture, although it is suited also to other feeds, such as di*iso*butylene and tri*iso*butylene. The hydrogenation process operates in the vapor phase, and is distinctive in that it employs low pressures (between 1 and 4 atmospheres, [392°F.] gage) and a temperature normally below 200°C. These mild conditions of temperature and pressure are applicable as a result of developing a suitable active nickel catalyst which will hydrogenate octene vapors as they are passed over it with the consumption of only a small stoichiometric excess of hydrogen.

The practicability of the process developed is shown by the fact that since 1935 the Shell Companies in the United States have produced more than 10,000,00 gallons of octanes (of 98-100 octane number) using this process.

APPLICATION OF PROCESS

From thermodynamic data, the conversion of octenes to octanes may be accomplished completely and readily by passing a mixture of octene and hydrogen over a suitable catalyst at atmospheric pressure and temperature. Parks and Todd[3] have discussed the thermodynamics of the reaction producing 2,2,4-trimethyl pentane from di*iso*butylene:

$$C_8H_{16}\ (\text{liquid}) + H_2 \rightarrow C_8H_{18}\ (\text{liquid}),$$

and have chosen the following values for the heat of reaction and the free energy change:

$$\Delta F^\circ_{298} = -20{,}280 \text{ cal. per g.-mol.}$$
$$\Delta H^\circ_{298} = -28{,}470 \text{ cal. per g.-mol}$$

The relation of temperature to the free energy of this reaction is equated as follows (assuming a linear relationship):

$$\Delta F^\circ = -28{,}470 + 25.7T.$$

For the production of gaseous *iso*octane, the relation is:

$$\Delta F^\circ = -28{,}570 + 27.6T,$$

which shows that the vapor reaction is thermodynamically feasible at temperatures below about 750° C. [1372°F.]. At temperatures in the region of 200°C. [392°F.] it is highly exothermic, and the free energy

change is decidedly negative. Therefore, in the presence of a suitable catalyst the reaction is highly complete at low pressure, a high partial pressure of hydrogen being unnecessary to effect complete hydrogenation of an octene feed.

While thermodynamic values for the conversion of octenes other than di*iso*butylene would not be equal to those values shown, the order of magnitude would be the same, and the general conclusions stated will hold for the other octenes as well.

Although the process developed is applicable to the hydrogenation of various olefinic materials, it has been utilized most extensively for the hydrogenation of a mixture of octenes prepared by sulfuric-acid polymerization of butylenes. The octene mixture is the result of interpolymerization of *iso*butylene and normal butylenes, and consists of several isomers, among which are 2,2,4-trimethyl pentenes 1 and 2. (This octene mixture yields a hydrogenated product which needs no additional treatment prior to blending into fuels.) In spite of the co-polymerization of normal butylenes, which enhances the octene yield, the octanes produced therefrom are only 1 to 2 octane numbers lower than pure 2,2,4-trimethyl pentane, and possess blending octane numbers practically equivalent thereto.

Concerning the applications of this process to the hydrogenation of other olefins, the production of *iso*dodecane from tri*iso*butylene has been carried out on a large scale. The equipment and operating conditions are identical with those required for octane manufacture, except that a converter temperature increase to 250°C. [482°F.] and an increased hydrogen-olefin mol ratio in the converters have been found to be most practical.

TEMPERATURE AND PRESSURE

The choice of operating pressure and temperature was made after extended investigation; a temperature of 180-190° C. [356-374° F.] and a gage pressure of 1 to 4 atmospheres have been found to be most practical. At operating temperatures substantially below 180° C. [356° F.], the rate of reaction is low, and the presence of small amounts of carbon monoxide in the hydrogen feed produces de-activation of the nickel catalyst through the formation of nickel carbonyl. Increasing temperature encourages thermal decomposition of the octene-fraction components, with a resulting decreased yield of octane and increased consumption of hydrogen. The increased consumption of hydrogen results from the hydrogenation of lower-boiling olefins produced in the decomposition, although the decomposition may result in higher-boiling olefins as well. Further, thermal decomposition normally produces some free carbon as well, which deposits on the catalytic surfaces and renders them inactive.

The pressure applied to the system is only that sufficient to maintain good plant control. The use of high pressures is not desirable, particularly with highly-active catalysts, inasmuch as the effect is to compress the reaction into a smaller volume of catalyst, with resultant overheating and consequent deterioration of the active surfaces.

THE CATALYST

The catalyst developed consists of activated nickel supported on porcelain. The unformed catalyst is a hydrated nickel nitrate impregnated in porcelain. The nitrate is decomposed to nickel oxide, and then reduced to metallic nickel in a stream of hydrogen. Hydrogen may be conserved by supplying air until decomposition is complete, and introducing hydrogen for reduction only; but the use of hydrogen throughout enhances slightly the activity of the catalyst. After formation, the catalyst is maintained in a hydrogen atmosphere when not in service. Contact with air results in rapid oxidation and consequent loss of activity.

The activated nickel catalyst is susceptible to poisoning, particularly by sulfur. While carbon monoxide and oxygen produce temporary loss of activity, which can be restored by reactivation in place, sulfur produces permanent loss of activity. It is desirable, therefore, to maintain the sulfur content of the octene feed at a minimum. This can be accomplished by proper treatment of butylenes prior to polymerization. The catalyst mass effects substantially complete removal of all sulfur which is contained in the octene feed, producing octanes containing 0.0001 percent by weight of sulfur; and even after a catalyst loses its ability to promote hydrogenation, it still retains an affinity for sulfur. This retention of ability to remove sulfur is useful, inasmuch as a catalyst no longer able to effect hydrogenation can be used for pre-treating the octene feed in order to reduce its sulfur content before contact with the active catalyst. Proper treatment of butylenes before polymerization reduces the sulfur content of the octene feed to blow 0.002 percent by weight, and a pre-treatment with a spent catalyst reduces this figure on the average to 0.0005 percent or less. An octene feed treated in this manner then contains only enough sulfur to produce slow de-activation of catalyst. In the plant operation described hereinafter, 1000 gallons of finished *iso*octane are produced per pound of nickel charged to the catalyst chambers.

HYDROGEN SUPPLY AND UTILIZATION

The source of hydrogen for plant-scale operation is not of particular importance, provided the supply does not contain compounds injurious to the catalyst. Sulfur compounds normally associated with hydrogen gas are easily removed by simple treatment of the gas stream. In the experimental work leading to the development of this process both electrolytic hydrogen and mixtures of hydrogen and nitrogen containing about 75 percent hydrogen were used. Convenient sources of hydrogen are, for instance, the pyrolysis of natural gas and the dissociation of ammonia. A process for the production of cheap hydrogen, free of impurities which poison nickel catalysts, has been developed recently by the Shell Chemical Company. This gas contains 85 percent hydrogen, with only methane and nitrogen as impurities. Both methane and nitrogen are inert, and their presence in this amount is not objectionable in the process.

Although excess hydrogen is not imperative in producing a high degree of hydrogenation, when using single-stage operation a 10- to 15-percent excess is desirable in order to increase the rate of conversion and decrease the volume of catalyst necessary to produce a unit volume of *iso*octane. It has been found practical to conserve hydrogen either by means of a two-stage countercurrent flow system or by direct re-cycling of residue gas through a single-stage converter. When the supply of hydrogen is limited and its cost is an important item in the total cost of operation, a two-stage counterflow system is more economical. In a two-stage system the octene feed to the first converter is mixed with vent hydrogen from a second reactor, the second reactor receiving fresh hydrogen together with partially-converted octenes from the first reactor as feed. Vapor from the second converter is cooled to permit condensation of octanes. With a two-stage countercurrent system

a hydrogen utilization of 95 percent is readily obtained. A simpler arrangement has been developed for use if a hydrogen utilization efficiency of 85-90 percent is permissible. In this system a 10- to 15-percent excess of hydrogen is introduced with the octene vapor to a single-stage converter; the excess gas is compressed to remove *iso*octane; and 50-80 percent of the residual gas is recycled in order to increase the hydrogen-octene mol ratio in the reactors. In one instance of actual plant-scale practice, 80 percent of the residual gas volume is re-cycled; and under equilibrium conditions with about 12 percent theoretical excess of fresh hydrogen added, the re-cycle gas contains 80 percent mol hydrogen. The re-cycle increases the hydrogen-octene mol ratio in the converters from 1.12 to 1.37 in this instance. The recycling operation effects a hydrogen saving of 5-10 percent in this plant operation.

SINGLE-STAGE VS. COUNTERFLOW SYSTEM

To show the advantage of a two-stage system in conserving hydrogen, data from two comparable laboratory experiments with single- and two-stage operation are shown in Table 1. (While plant-scale operation effects greater hydrogen utilization than in laboratory tests, the comparison of laboratory data is indicative.)

CATALYST REACTIVATION AND REGENERATION

The presence of small amounts of sulfur in the octene feed, together with octane decomposition and carbon deposition which accompanies the conversion, would necessitate frequent replacement of the catalyst. However, a method of reactivation has been developed which markedly increases catalyst life. When a catalyst decreases in activity to a certain point, as measured by the throughput capacity of a given volume of catalyst, reactivation in place is practiced. The catalyst bed is purged of hydrogen, and air then is introduced for from 4 to 12 hours, depending upon the condition and the quantity of catalyst. The oxidized catalyst again is reduced with hydrogen. Although the initial activity of the catalyst is not completely restored, applying the reactifying operation two to four times increases the life of a charge of catalyst by at least 150 percent. The activity declines slowly after each reactivation, however, and ultimately the catalyst charge is removed from the converters, and regenerated.

TABLE 1

Comparison of Hydrogen-Utilization Efficiency Single-Stage Vs. Countercurrent-Flow Operation

Experiment No. 1—Single-stage, 100-ml. catalyst (no gas re-cycle).
Experiment No. 2—Two-stage, 100-ml. catalyst in each stage (no gas re-cycle).
Olefin feed—di*iso*butylene.
Hydrogen feed—gas containing 75 percent by volume of hydrogen and 25 percent by volume of nitrogen.

	Experiment No.	
	1	2
Total liquid feed volume, liters	10.7	10.5
Total liquid product volume, liters	10.5	10.3
Unsaturation of product, percent by weight as C_8H_{16}	1.0	1.0
Product yield, percent by volume of feed	98	98
Hydrogen feed, liters as pure hydrogen	2,300	1,600
Mol ratio of hydrogen to di*iso*butylene in converters	1.5	1.06
Utilization of hydrogen, percent	67	94
Analysis of residual gas after condensation of octanes:		
C_nH_{2n}	0.0	0.5
H_2	44.3	12.3
C_nH_{2n+2}	7.6 (n=3.8)	6.3 (n=2.7)
N_2	48.1	80.9
Volume of residual gas, liters	1,600	660

EQUIPMENT FOR PLANT-SCALE OPERATION

The equipment required for plant-scale operation of the hydrogenation process is shown in Figures 1, 2, and 3. These figures are skeleton flow diagrams which show only the major pieces of apparatus.

The principal problem in the design of the catalytic converters is that of heat removal. The heat of reaction, according to Parks and Todd[3], is about 450 B.t.u. per pound. In order to facilitate rapid heat transfer, the catalyst is contained in 3-inch diameter vertical tubes, arranged in bundles by rolling the tubes into end plates, with circulating hot fluid maintained around the tubes. The circulating hot fluid is carried at the desired reactor temperature, and is led from the reactors through a cooler, with a controlled by-pass—maintaining thereby a constant temperature on the hot fluid to the converters. For catalyst formation and reactivation, which are carried out at higher temperatures, a separate hot-fluid circulating system supplied with a furnace is used. Where several converters are in use, it is possible thereby to retain some in service while others are being subjected to catalyst formation or treatment.

Heat to the hydrogen heater and octene vaporizer is supplied directly by means of hot fluid. The hydrogen

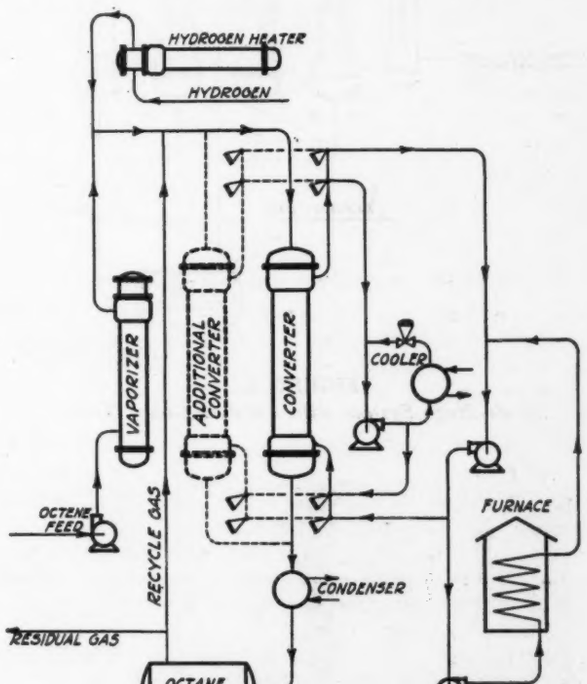


FIGURE 1
Single-Stage System

and octene vapors are supplied to the converters at a temperature of not above 200°C. [392°F.].

It is apparent that some heat exchange can be effected within the system, the extent of this exchange being determined by the economics of heat supply. With a single-stage converter the one simple heat exchange is that between the converted gas stream and octenes being fed to the vaporizer. Two heat exchanges are available in a countercurrent system, one on each converter.

Deterioration of equipment due to corrosion is negligible. Due to the low temperatures and pressures

employed, no special alloys or materials are necessary in the major pieces of equipment. No parts of the equipment suffer an abnormal rate of wear or deterioration.

OPERATION OF PLANT-SCALE PROCESS

The operation and control of the hydrogenation system are simple. The primary point of control is the unsaturation of the finished product, as determined by titration with a weak brominating agent.

The use of catalyst guard tubes is advantageous for sulfur removal and, consequently, catalyst conservation; but normally the guard catalysts are not effective in promoting hydrogenation themselves. The total feed hydrogen can be introduced into the octene vapors prior to passing through the guard tubes, but the large amount of hydrogen is not necessary in effecting sulfur removal. Therefore, the major portion of the feed hydrogen may be introduced following the guard tube, thereby increasing the contact time of a unit weight of octenes

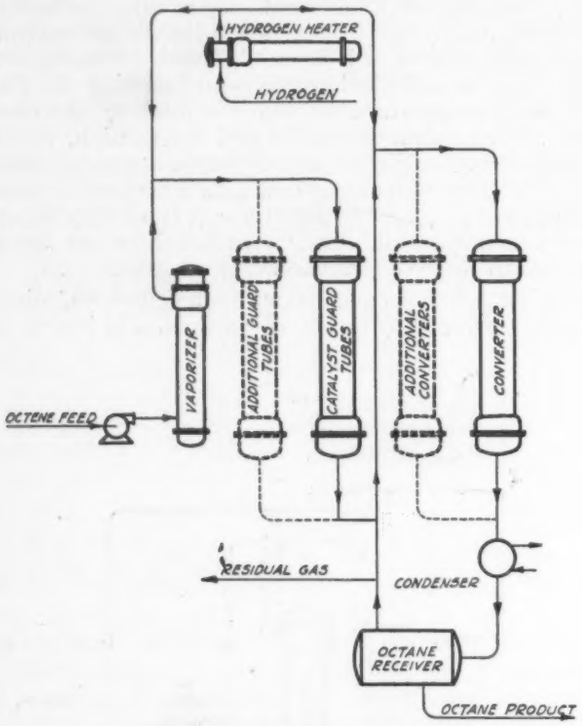


FIGURE 2
Single-Stage System with Catalyst Guard Tubes

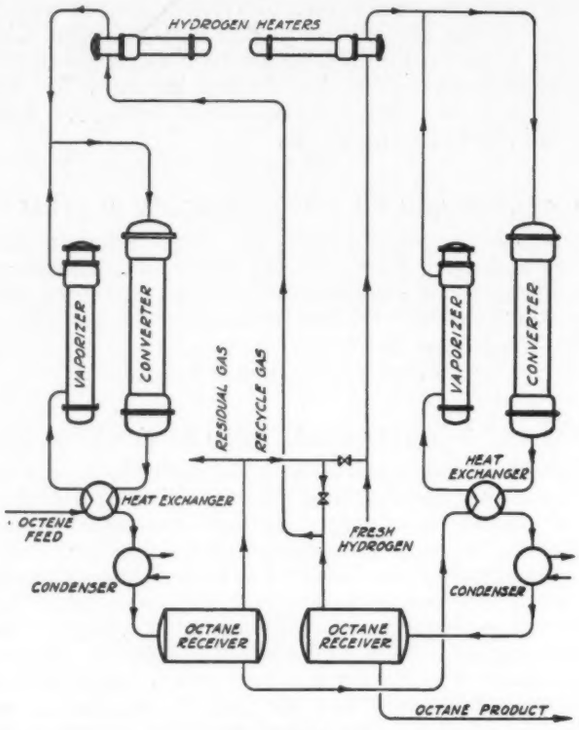


FIGURE 3
Two-Stage Countercurrent System

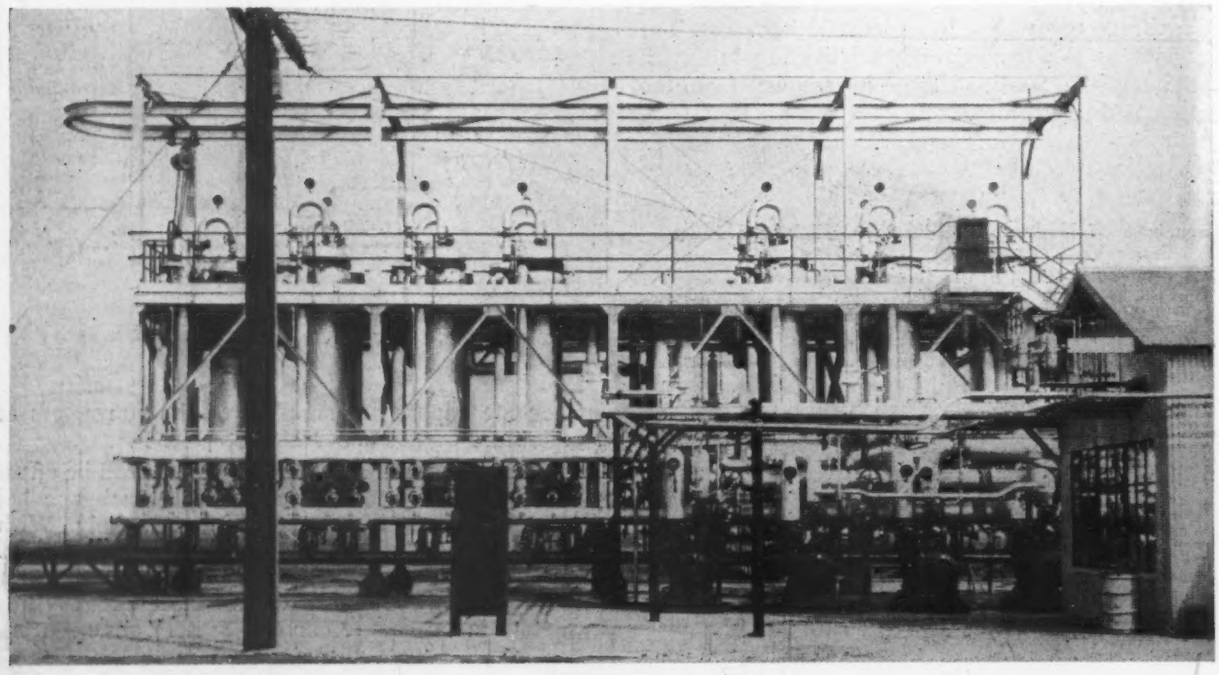


FIGURE 4
Catalytic Hydrogenation Plant, Shell Oil Company, Dominguez, Calif.

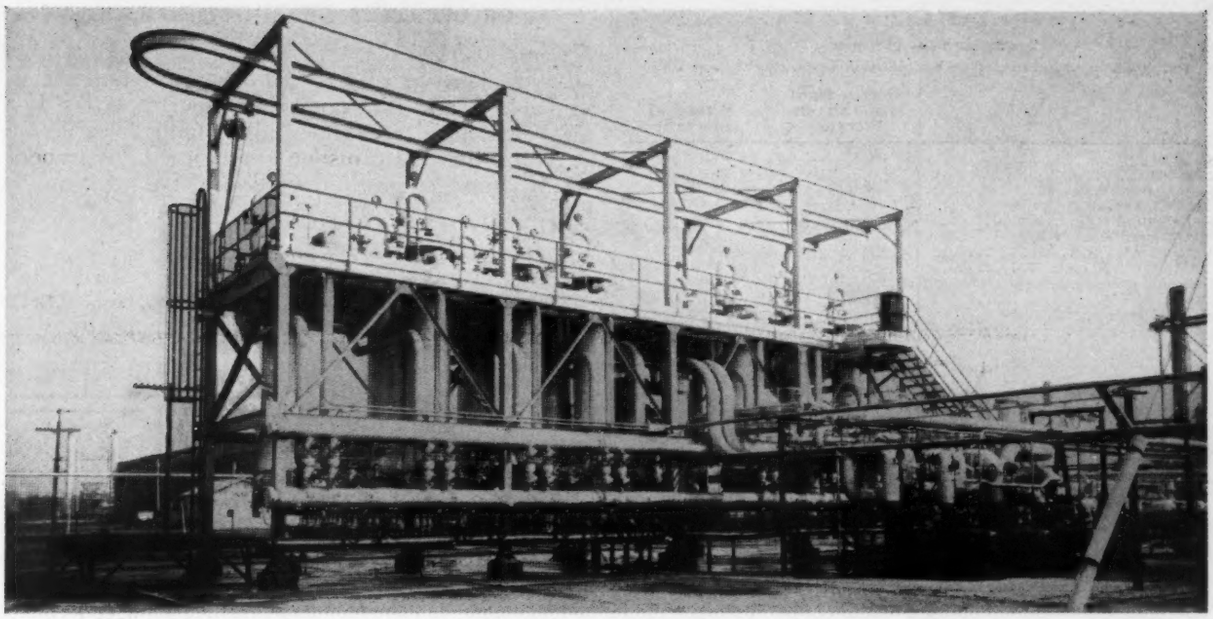


FIGURE 5
Catalytic Hydrogenation Plant, Shell Oil Company, Dominguez, Calif.

in the guard tube chamber. As a rough guide, one volume of guard catalyst is sufficient for two volumes of active catalyst.

A feature which has been incorporated in some plants is the inclusion of a catalyst tube for hydrogen feed to convert traces of carbon monoxide to methane and water. This hydrogen guard tube eliminates the possibility of nickel-carbonyl formation on cold spots in the catalyst bed. However, this added precaution is not necessary in most cases. The presence of water vapor is not injurious to the active nickel catalyst. (Normally steam is used for purging the system of either air or hydrogen.)

At the Wilmington, California, refinery of Shell Oil Company a hydrogenation plant has been in operation for 22 months. During this period the yield of finished octanes has averaged 103.1 percent by volume of the octene feed. (The theoretical yield of 2,2,4-trimethyl pentane is 105.5 percent by volume of di*iso*butylene charged.) A conversion of 99 percent is easily attained, although values higher than this necessitate slightly increased apparatus sizes. The Wilmington plant, a single-

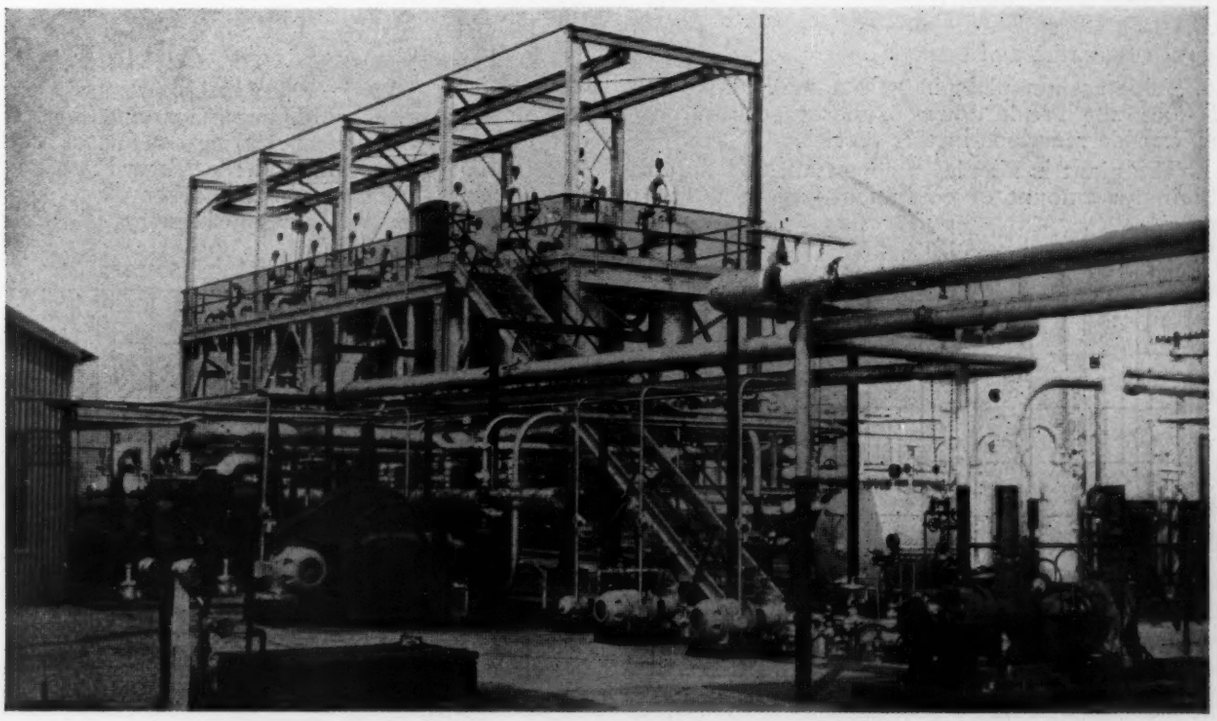


FIGURE 6
Catalytic Hydrogenation Plant, Shell Oil Company, Dominguez, Calif.

TABLE 2
Properties of Octane

	Octane from Mixed Octene Fraction	Technical Isooctane
Gravity, API	66.3	70.9
Color, Saybolt	30+	30+
Reid vapor pressure, lb	2.6	2.1
Unsaturation, percent by weight	1.1	1.8
Copper-dish gum, mg. per 100 ml	1	1
Accelerated gum, mg. per 100 ml	1	1
Wright acid heat, ° F	26	23
Navy acid heat, ° F	7	3
Sulfur (nephelometric), percent by weight	0.0001	0.001
Octane No., ASTM	98.2	99.7
ASTM Distillation, ° F.		
Initial boiling point	196	205
Dry point	236	235
10-percent point	221	210
30-percent point	225	210
50-percent point	227	212
80-percent point	230	214
90-percent point	231	215
95-percent point	233	216
Distilled, percent by volume	99	99

stage system, has obtained 86-89 percent utilization of hydrogen while producing 99 percent saturated product. Other plans using two-stage countercurrent flow have realized 95 percent hydrogen utilization. Using catalyst guard tubes in series with the converters, the life of a catalyst is 1000 gallons of finished product per pound of nickel in the catalyst bed. With a catalyst recovery plant the cost of catalyst is not that of replacement but, instead, only for reprocessing the spent catalyst. The figure of 1000 gallons per pound of nickel is attained with an average of three reactivations with air carried on *in situ*.

PROPERTIES OF FINISHED OCTANE

Some average properties of finished octane prepared by hydrogenation of a mixed octene fraction are shown in Table 2, and for comparison the properties of technical *iso*octane are given also. (Small variations in gravity, distilaltion, octane number, etc., of octane will result from changes in operation of the plant producing butylene polymers.)

PATENTS

General features of the Shell process as described are covered by patents and patent applications in the United States and abroad.

CONCLUSION

A catalytic hydrogenation process has been developed by the Shell Companies which is simple, economical, and particularly adapted to the hydrogenation of octenes produced by polymerization of butylenes. The process operates at low pressure (below 4 atmospheres, gage) and at a temperature not exceeding 200° C. [392°F.].

The process effects substantially complete hydrogenation, and produces thereby high-octane fuels low in acid-heat number and ideally suited for the manufacture of high-octane aviation gasoline.

BIBLIOGRAPHY

[1] D. P. Barnard, *SAE Journal*, 41, 415-20 (1937).
[2] *Proc. API* 18 [III] (1937), and *Refiner* 16, 493-6 (1937).
[3] *Ind. Eng. Chem.* 28, 418-9 (1936).

Shell Process

[*Continued from page 247*]

vantage in many locations where steam is not available, or where an inexpensive fuel makes this type of regeneration more economical.

9. It is a self-operating process requiring a minimum of regulation and control tests.

10. Tripotassium phosphate is a very stable salt, and does not break down or decompose through complex side reactions in this service.

11. The plant is simple to construct, and requires a minimum amount of equipment—all of which is standard.

12. The maintenance cost is low.

PATENTS

The process is covered by U. S. Patents 1,945,163 and 2,110,403, assigned to the Shell Development Company. Other patents are pending.

COMMERCIAL INSTALLATIONS

At present (March, 1938) installations are operating in the Martinez and Dominguez refineries of Shell Oil Company, the East Chicago refinery of Shell Petroleum Corporation, and the Norwalk refinery of the Wilshire Oil Company. Another plant is under construction at the Watson refinery of Richfield Oil Company.

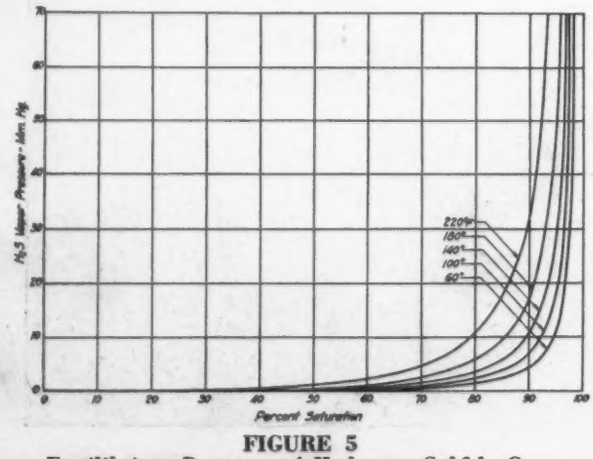


FIGURE 5
Equilibrium Pressure of Hydrogen Sulfide Over 20 Percent Tripotassium-Phosphate Solution.

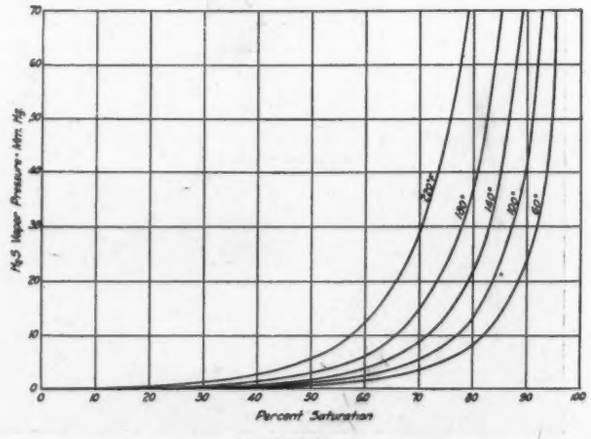


FIGURE 6
Equilibrium Pressure of Hydrogen Sulfide Over 50 Percent Tripotassium-Phosphate Solution.

Application of Bailey's Theory to Tube-Stress Calculations

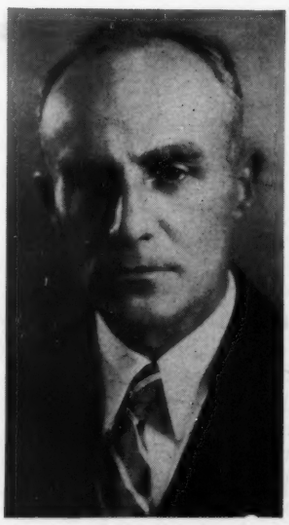
C. O. RHYS
Standard Oil Development Company
Elizabeth, New Jersey

THIS paper discusses the applicability to refinery tube-stress calculations of Bailey's theory of metal subjected to creep. The frequent fallacy of temperature-stress calculations based on the assumption of elastic material is discussed; and the effect of heat input on a tube, subjected to internal pressure and undergoing creep, is explained. Formulas and charts for use in practical calculation are given. Derivations, data, and illustrative numerical examples appear in the appendix.

Presented at Eighth Mid-Year Meeting, American Petroleum Institute, Lassen Hotel, Wichita, Kansas, May 25, 1938.

TUBES and hollow cylinders in refinery equipment are subjected to stresses set up by heat transfer and pressure. Up to about a year ago the Standard Oil Development Company's procedure for determining such stresses was based on the theory of Lorenz[1] for temperature stresses, and the well-known Lame thick-cylinder formula for pressure stresses.

The Lorenz theory applies to stresses in a tube of elastic material, and of uniform strength throughout the wall, subjected to heat transfer. These conditions are realized only for moderate metal temperatures, where there is considerable elasticity, little change in strength due to the temperature drop, and negligible stress relief due to the very slow creep rate. For high metal temperatures, however, which are accompanied by little elasticity, considerable change in strength for a small temperature drop, and a high creep rate, the Lorenz theory is unsuitable, while that of R. W. Bailey[2] applies.



C. O. RHYS

C. O. Rhys was born in London, England, and handled designing work for Globe Pneumatic Engineering Company in London before coming to the United States in 1910, to spend three years with William Cramp & Sons Ship and Engine Building Company. During 1913 he did engine and boiler testing work for Bowers Southern Dredging Company at Galveston, and until 1918 designed machinery for Diamond Match Company, and then became associated with United Shoe Machinery Company in the experimental department. In 1922 he joined the faculty of Georgia School of Technology at Atlanta, Georgia.

Going with Standard Oil Company of New Jersey in 1924, currently he is in the process engineering department of Standard Oil Development Company at Elizabeth, New Jersey.

ELASTIC TEMPERATURE STRESSES—EFFECT OF DUCTILITY

For the conditions specified, the temperature stresses as calculated by the Lorenz theory, undoubtedly exist. In materials like cast iron and glass, which are elastic up to the breaking point, they cause fracture—as in the cases of unequal cooling in castings and boiling water poured into glass vessels. In a material such as steel, however, with a considerable range of ductility preceding the breaking point, temperature stresses, within this range, disappear as soon as the plastic deformation due to thermal expansion has taken place. A deformation in the ductile stage sufficient to cause rupture would require a heat input far beyond what is likely to exist in refinery practice. This is illustrated by heat inputs of 100,000 B.t.u. per square foot per hour and higher, which commonly occur in the steel tubes of boilers, and is also borne out by data from a number of tubes tested to destruction by the Standard Oil Development Company. In every case the stress, as calculated by Bailey's theory, for the heat input and bursting pressure was extremely close to the breaking stress of the material at the test temperature. Had the stresses, as calculated on the elastic basis, actually been in existence, the bursting pressures would have been from 20 to 50 percent less than they actually were.

From the above it might seem that, in tube calculations, only the stresses due to pressure need be can-

sidered, and in boiler design—with temperatures from 600 to 700°F.—this is actually done. In this temperature range the elastic characteristics predominate, and the creep rate is negligible. Even such a low creep rate as 0.1 percent per 100,000 hours corresponds with a stress which is above the elastic limit; and, therefore, creep cannot well be used as a basis for the working stress. Tubes are proportioned by the thick-cylinder formula (or its equivalent), and the working stress is some fraction—roughly about a third—of the elastic limit. Designed on this general basis, tubes are found to withstand satisfactorily the effects of very high heat inputs.

APPLICABILITY OF BAILEY'S THEORY

In refinery equipment, particularly in cracking-coil work, where the temperature range is from 900 to 1,200°F., high creep rates exist even at low stresses. The consequent creep relief reduces to negligible amounts any temperature stresses which may occur. Changes in metal temperature due to heat transfer, however, are accompanied by corresponding variations in metal strength, creep rate, and pressure stress through the tube wall. These factors, which are not taken into account in the Lorenz-Lame theories are of great importance in the 900- to 1,200°F. temperature range. They are included in the theory developed by Bailey.

In general furnace work, the tube thickness required for the high metal temperature will govern design; in fact, for most practical cases, the tube found for the high-temperature end of the furnace will be about right for the low-temperature end. This can be seen from the following calculation, which represents about an average case:

Consider a coil outlet tube, 4 inches in outside diameter, with a heat input of 10,000 B.t.u. per foot of length per hour, and a pressure of 1,000 pounds per square inch; allowable metal temperature, 1,100° F. From Figure 1,* the temperature drop is 26 degrees. From the formula on the chart, **K**, the ratio of outside diameter to inside diameter is found to be:

$$\text{Log. } K = \frac{120 \cdot 26}{10{,}000}$$

$$K = 1.37$$

By means of Figure 2,* the maximum stress in this tube equals

$$\frac{1{,}000}{0.37 \cdot 0.87}$$

or 3,200 pounds per square inch at the inside wall, corresponding with a creep rate of 0.1 percent per 100,000 hours.

Next suppose that, at the entrance to the radiant section, the metal temperature is 875°F. Here the creep stress and the elastic limit are both about 12,500 pounds per square inch. Take the pressure as 1,200 pounds per square inch. Then, by the thick-cylinder formula, the stress due to pressure is

$$\frac{1{,}200 \cdot 2.87}{2.37 \cdot 0.37}$$

which equals 3,900 pounds per square inch, or about a third of the elastic limit. Supposing all the conditions to be right for the continued existence of elastic temperature stresses (perfect elasticity, no creep relief, etc.) a heat input of 25,000 to 30,000 B.t.u. per square foot per hour would be required before the ductile stage was reached—and it is doubtful if at 875° the necessary conditions are even approximated.

*See stress calculations given in detail in the appendix.

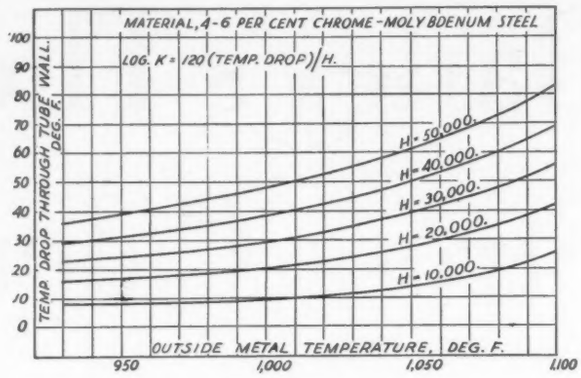


FIGURE 1

The above is given as an illustration that a tube determined by Bailey's theory for the high-temperature region of a furnace is generally safe for other locations.

BAILEY'S THEORY

The theory presented by R. W. Bailey in his paper "The Utilization of Creep-Stress Data in Engineering Design," read before the Institution of Mechanical Engineers, London, November 1935, includes the case of a tube undergoing creep and subjected to heat input and internal pressure. As shown later, in the appendix, there can be derived from this the formula:

$$K^{2N'} = \frac{f'}{f' - \frac{P}{AN'}} \qquad \text{.....(a)}$$

which gives the relationship between stress, pressure, heat input, and tube proportions.

Where:

A=a constant depending on the material.
f'=working stress, determined by allowable creep rate and metal temperature.
K=ratio $\frac{\text{outside diameter}}{\text{inside diameter}}$.
N'=a quantity found from the heat input (see appendix).
P=internal pressure.

From this formula it can be seen that the quantities described as important in the preceding section—heat transfer, metal temperature, creep rate—enter into the formula for designing the tube.

It will be observed that the modulus of Poisson's elasticity and Poisson's ratio do not appear in the formula. These quantities do occur in temperature-stress calculations which are based on the assumption of an elastic material. Their absence removes a source of error, as they are very difficult to determine accurately for tube metals, especially at high temperatures.

By means of the formulas and charts given in the appendix, the proper thickness of tube wall can be determined in a simple and direct manner, without having to resort to cut-and-try methods. Examples are given which illustrate the procedure. The time saved in calculation by the avoidance of trial-and-error methods, inseparable from the use of the Lorenz-Lame formulas, has been noteworthy.

SUMMARY

The general purport of this paper is to show the compatibility of R. W. Bailey's theory of creep stresses with the general operating conditions of tubes in refinery equipment.

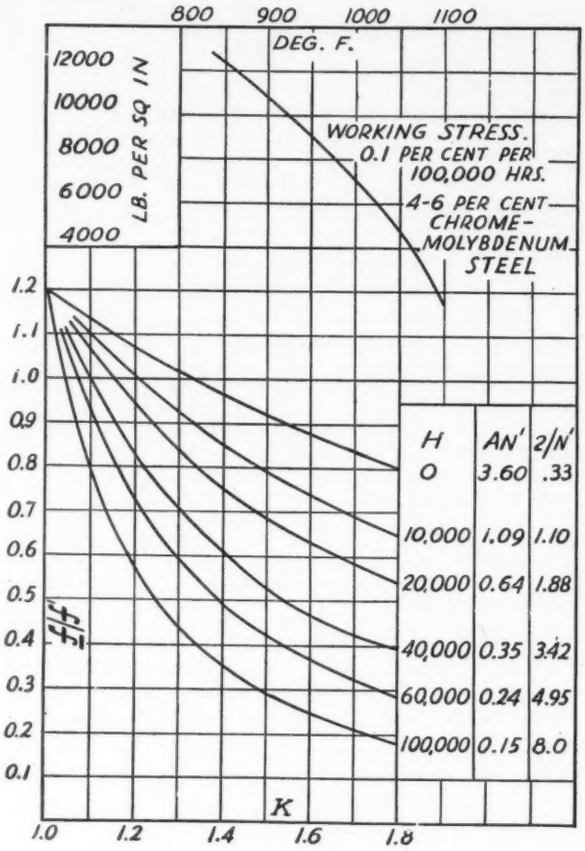


FIGURE 2

In the introduction it is pointed out that, before the advent of Bailey's theory, a method of calculation, based on the combined work of Lorenz and Lame, was used. This method applies only to conditions which do not include the cases of high metal temperature and high creep rate occurring in cracking-coil work. For such cases the method of Bailey, based on creep phenomena, is much more suitable.

Elastic temperature stresses are then discussed. It is explained that they cause fracture only in materials which are elastic up to the breaking point—like glass and cast iron. Where there is a considerable range of ductility—as in most tube material—it is practically impossible for rupture to occur due to temperature stress. Reference in support of this is made to current boiler practice and to destruction tests carried out by the Standard Oil Development Company. Why, in spite of this, furnace tubes cannot be designed on a basis of pressure stress only is explained by considering the effect of heat transfer on pressure-stress distribution and metal-strength variation through the tube wall. A numerical example is given, showing that high-metal-temperature conditions govern tube design.

The form of equation most suitable for tube-stress calculations is next presented. The factors most important in high-temperature metal subjected to heat input and internal pressure enter into it. As it is derived on a basis of creep and not elasticity, Young's modulus and Poisson's ratio are not included. This removes a source of error, as these quantities are very difficult to determine for hot metal. The equation is of such a form that, for a known working stress, the tube proportions can be found directly without any cut-and-try methods. This saves a considerable amount of time in determining tube sizes.

The appendix contains the derivation of formulas, illustrative charts, with data for their preparation, and numerical examples showing the use of the formulas and curves.

APPENDIX

The paper, "Utilization of Creep-Stress Data in Engineering Design," R. W. Bailey, read at the Institution of Mechanical Engineers, London, November 22, 1935, gives a very full treatment of the relationship between stress and creep rate. Applications to important engineering parts are dealt with, including the case of thick tubes subjected to internal pressure and heat input.

In this paper, sets of curves are given for the ratios:

$$\frac{\text{Mean hoop stress}}{\text{Inside hoop stress}}\left(\frac{f}{f'}\right) \text{ and } \frac{\text{outside diameter}}{\text{inside diameter}} K,$$

together with full instructions and examples for calculating tube proportions (see below).

These sets of curves are computed from the equation appearing on page 38 of the above paper and fully derived in Appendix V, page 116, of the paper. With the numerical values inserted the equation becomes:

$$\frac{f}{f'} = \frac{AN' \left(K^{\frac{2}{N'}} - 1\right)}{K^{\frac{2}{N'}} (K-1)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

For KA2S $A=0.555$ $N' = \dfrac{12}{1+\dfrac{H}{2{,}820}}$

For chrome-molybdenum steel $A=0.6$ $N' = \dfrac{6}{1+\dfrac{H}{4{,}320}}$

For steel $A=0.6$ $N' = \dfrac{6}{1+\dfrac{H}{5{,}900}}$

For NCT3 $A=0.555$ $N' = \dfrac{12}{1+\dfrac{H}{2{,}000}}$

H=heat input in B.t.u. per foot of length per hour.

Equation (1) is illustrated by the curves in Fig. 2, which are plotted for the ratio $\frac{f}{f'}$ against K for different values of the heat input H. Values of AN' and $\frac{2}{N'}$ are also given, which are of assistance in using equations (2) and (3).

As Figures 1 and 2 appear to a small scale, it is advisable to re-plot them to a convenient size for practical work. Fig. 1 and 2, as presented, are for 4-6 percent chrome-molybdenum steel. Data for plotting such curves for this and other materials accompany equation (1).

The mean hoop stress f is the pressure multiplied by the internal radius and divided by the thickness, or:

$$f=\frac{Pr'}{r^0-r'}=\frac{P}{K-1}, \quad \text{where } K=\frac{r^0}{r'}.$$

Substituting this for f in equation (1):

$$f'=\frac{PK^{\frac{2}{N'}}}{AN'(K^{\frac{2}{N'}}-1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

By transposing equation (2):

$$K^{\frac{2}{N'}}=\frac{f'}{f'-\frac{P}{AN'}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

This is equation (a) appearing previously in this paper. The temperature drop through the tube wall is given by the equation:

$$T-T''=\frac{6H}{\pi k}\cdot \log.\ K \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where T and T'' are the outside and inside metal temperatures in deg. F., and k is the conductivity of the metal in B.t.u. per sq. ft. per deg. F. per hour per inch of thickness. Substituting in equation (4) from equation (3), there results:

$$T-T''=\frac{3HN'}{\pi k}\cdot \log.\frac{f'}{f'-\frac{P}{AN'}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

This is the equation from which the curves in Fig. 1 are plotted. k is determined by the material—being 150 for KA2S, 230 for chrome-molybdenum steel, and 310 for steel. For A and N' see values under equation (1).

A set of values of T'' is taken in the required temperature range. Corresponding values of f', equal to the allowable working stress, are known from existing creep-stress data (see curve in upper part of Fig. 2).

Values of $T-T''$ are then calculated from equation (5). These added to the values of T'' give values of T, so that a curve for T and $T-T''$ can be plotted.

The formula in Fig. 1 is equation (4) with the value of k for the 4-6 percent chrome-molybdenum steel incorporated.

TUBE-STRESS CALCULATIONS BY BAILEY'S THEORY

The relations between hoop stress, pressure, heat input, and tube proportions are expressed by the equation:

$$K^{\frac{2}{N'}}=\frac{f'}{f'-\frac{P}{AN'}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (a)$$

A=a constant depending on the material. It is 0.6 for chrome-molybdenum steel and for steel, and 0.555 for KA2S.

f'=The safe working hoop stress at the tube bore, taken as the stress accompanying a creep rate of 0.1 percent per 100,000 hours. This depends on the inside wall temperature. A curve of f' for 4-6 percent chrome-molybdenum steel is given in Fig. 2.

K=ratio $\frac{\text{outside diameter}}{\text{inside diameter}}$

N'=a quantity depending on the heat input H.

Values of AN' and $\frac{2}{N'}$ are given in Fig. 2.

H=heat input in B.t.u. per foot of tube length per hour.

When the metal temperature at the inside wall, the heat input, and the internal pressure are known, the ratio K can readily be calculated from equation (a). As an example, take 1,045 deg. F., 20,000 B.t.u. per foot per hour and 1,200 lb. per sq. in. Taking the required quantities from Fig. 2:

$$K^{1.88}=\frac{4,600}{4,600-\frac{1,200}{0.64}}$$

$$K=1.32.$$

From the formula for the relations between H, K, and the temperature drop given in Fig. 1 the drop through the wall is found to be:

$$\text{Temp. drop}=\frac{H\cdot \log.\ K}{120}=\frac{20,000\cdot \log.\ 1.32}{120}=47 \text{ deg.};$$

so that the outside wall temperature is 1,045+47=1,092 deg.

Supposing the outside temperature had been known as 1,100 deg., instead of the inside temperature, and it had been required to design a tube for the other conditions. f' cannot be found until the inside wall temperature is known, and to find this requires K. For this purpose the curves in Fig. 1 can be used. Drop through the tube wall is plotted against outside wall temperature for different values of H. All the curves are based on an internal pressure of 1,000 lb. per sq. in., but for other pressures the drops will be very nearly in proportion.

In the present example, H=20,000, and outside metal temperature=1,100 deg. The drop through the wall is found to be 42 deg. at 1,000 lb. per sq. in. At 1,200 lb. per sq. in. it will be $\frac{42\cdot 1,200}{1,000}=50$ deg. Using the formula accompanying the curves:

$$\text{Log. } K=\frac{50\cdot 120}{20,000}$$

$$K=1.35.$$

To see whether this will give the proper stress at the tube bore, where the temperature is 1,100—50=1,050 deg., the set of curves in Fig. 2 for $\frac{f}{f'}$ and K can be used. f is the mean hoop stress. f', already referred to as the safe working stress, is that stress which will produce a creep of 0.1 percent per 100,000 hours in simple tension.

The mean hoop stress is first found by the well-known relation:

$$f=\frac{P}{K-1}=\frac{1,200}{0.35}=3,430 \text{ lb. per sq. in.}$$

From the curves it is seen that for K=1.35, H=20,000, the stress ratio $\frac{f}{f'}=0.79$, or $f'=\frac{3,430}{0.79}=4,350$ lb. per sq. in. A reference to the temperature-stress curve in the upper part of Fig. 2 shows 4,400 lb. per sq. in. to correspond with 1,050 deg., as nearly as can be read.

The stress can also be checked by using equation (2):

$$f'=\frac{PK^{\frac{2}{N'}}}{AN'(K^{\frac{2}{N'}}-1)}=\frac{1,200\quad 1.76}{0.64\cdot 0.76}=4,350 \text{ lb. per sq. in.},$$

which is in agreement with the result obtained by the other method.

BIBLIOGRAPHY

[1] Dr. Ing. Rudolph Lorenz, "Temperaturspannungen in Hohzylinder," z. *Ver. deut. Ing.* (1907).

[2] R. W. Bailey, "The Utilization of Creep-Stress Data in Engineering Design," *Proc. Inst. Mech. Eng.* (*London*) (1935).

New Developments in Petroleum-Storage Vessels

D. E. LARSON
Chicago Bridge & Iron Company, Chicago

NATURAL petroleum resources can be employed most advantageously by enabling the motorist to secure increased mileage from each barrel of crude oil produced. The automobile and petroleum industries are working toward this end by developing fuel systems capable of utilizing more efficient fuels of higher volatility, and by perfecting refining and blending processes for producing superior motor fuels, with the elimination of practically all waste products.

These advances must be supplemented by efficient methods for storing and handling the products involved. The trend toward higher vapor pressures emphasizes the economic necessity for vessels designed to store volatile liquids without deterioration or loss by evaporation.

Methods commonly employed for reducing losses from volatile liquids include elimination of air circulation in the vapor space, reduction of temperature variation, elimination of vapor space, the use of variable vapor space, and storage under pressure. Well-known applications of these methods are the use of gas-tight fixed roofs with conservation vents, reflecting paints, water-top roofs, water-spray systems, insulated roofs, sunshades, breather roofs, lifter roofs, water-displacement systems, floating roofs, and pressure vessels.

More recent developments include the use of improved floating roofs for working tanks, balloon systems for existing storage tanks, balloon roofs for marketing tanks, and Hortonspheroids for a wide range of volatile products including all motor fuels and natural gasolines.

Presented at eighth mid-year meeting, American Petroleum Institute, Wichita, Kansas, May 25, 1938.

The statements and opinions expressed herein are those of the author, and should not be construed as an official action or opinion of the Institute nor of this publication.

MUCH has been written about the conservation of natural resources, particularly with regard to crude petroleum. True conservation is achieved when the motorist is able to secure the maximum possible mileage from each barrel of crude oil produced. This can be accomplished only through the joint cooperation of automobile manufacturer, refiner, marketer, and storage-tank fabricator.

The automotive engineer, by establishing a trend toward lower-temperature fuel systems, is making it possible to utilize the more volatile fuels now available, which give better performance and higher efficiency. The refinery technologist is effecting tremendous potential savings by developing new processes for converting former waste hydrocarbons into high-grade motor fuels. By improving the design of storage vessels, the tank fabricator is solving the problem of storing volatile products without excessive loss due to leakage or evaporation.

NEW PROCESSES NECESSITATE IMPROVED STORAGE

When an industry engaged in manufacturing finished products from raw materials is in the earlier stages of development, waste products are usually plentiful, and conservation is neglected. As the industry becomes better established, however, the possibility of increasing profits through the utilization of these waste materials is investigated, and technical developments may elevate some of them to positions of prime importance. This has been true in the oil industry. During recent years new refining processes and improved blending methods have made it possible to use the more volatile hydrocarbons in the production of superior motor fuels. The necessity for preserving these light constituents, which were formerly wasted, has stimulated an extensive search for more efficient methods of storing petroleum products. Some of the more outstanding developments necessitating the adoption of improved storage facilities are described briefly in the following paragraphs.

POLYMERIZATION

This process provides the refiner with a means for partially converting butane and propane into motor fuel having a normal gasoline boiling range. In the past many of the oil companies followed the practice of allowing these fractions to evaporate from crude oil in field storage tanks. There was no object in retaining constituents which had to be disposed of at the refinery. The increasing use of polymerization has made it profitable to store crude oil in containers capable of retaining the lighter hydrocarbons.

NATURAL GASOLINE

Motor fuels made by blending natural gasoline with suitable refinery stocks are superior to straight-run gasolines in easy starting properties and anti-knock characteristics. The popularity of these blends has caused a tremendous increase in the consumption of natural gasoline. The demand for this product varies with the seasons. It is greatest in the fall when blending stocks for winter gasolines are needed, and lowest in the spring when the need for easy starting properties has passed. In order to meet the peak demand, large quantities of natural gasoline must be placed in storage during the summer. Because of its high vapor pressure,

D. E. LARSON

The author of this paper was graduated by Oregon State College in 1928 with the degree B.S. in Civil Engineering. From 1928 to 1930 he was research graduate assistant in the experiment station at the University of Illinois where he majored in structural engineering and was granted the degree of M.S. in 1930. Employed by Chicago Bridge & Iron Company in 1930, he served as assistant engineer in the research department and consultant on technical sales problems in the sales department. Currently, he is engineer in charge of development activities. He is a member of numerous scientific and technical societies.

this gasoline cannot be stored in conventional tanks without prohibitive evaporation losses. This has created a demand for pressure containers having capacities as high as 100,000 barrels and designed for working pressures up to 15 pounds per square inch, or more.

100-OCTANE AVIATION GASOLINE

At the present time the demand for 100-octane aviation gasoline is far in excess of the supply. Stocks of this material must be built up gradually, because large quantities cannot be manufactured within a short period of time. It is essential that such stocks be protected against deterioration by storing them in containers which effectively prevent evaporation loss and the accompanying decrease in physical characteristics.

IMPROVED MOTOR FUELS

In addition to the developments listed above, there has been a definite trend toward the marketing of motor fuels having improved anti-knock characteristics and easy starting properties. This has created a noticeable tendency toward the use of tankage that will reduce evaporation, and thus prevent decreases in octane rating and vapor pressure during periods of storage.

METHODS FOR INCREASING STORAGE EFFICIENCY

Losses from stored petroleum products occur either by leakage or evaporation, or by a combination of the two. Inasmuch as leakage can be eliminated by good workmanship, especially when welded construction is employed, the problem of conservation is principally one of dealing with evaporation. The history of progress in storage-tank development is the story of a series of successive attempts to reduce evaporation losses.

Evaporation is costly for two reasons: 1, because it results in the loss of a quantity of the material which could be marketed; and, 2, because the product which remains after vaporization is one of inferior physical characteristics. The fractions which provide the desirable properties in finished motor fuels are the ones with the higher vapor pressures which evaporate first.

A discussion dealing with new development in storage tanks would be incomplete without a brief resume of previous progress. The devices described in the following paragraphs are classified in accordance with the methods employed to reduce the loss.

ELIMINATION OF AIR CIRCULATION

If a storage-tank roof has open vents or seams that are not gas-tight, the air currents circulating in the vapor space whip up the vapors above the liquid surface and carry them out of the tank. Losses of this sort can be prevented by the use of gas-tight steel roofs equipped with pressure and vacuum valves that open only when a small amount of pressure or vacuum has formed. Although these vents effect no appreciable reduction in breathing or filling losses, the reduction in circulation loss alone is sufficient to repay their cost within a reasonably short period of time. Practically all tanks with fixed steel roofs are now equipped with conservation vents.

TEMPERATURE REDUCTION

Breathing losses in tanks equipped with gas-tight fixed roofs and conservation vent valves can be partly eliminated by providing an insulating or reflecting medium for decreasing the daily temperature variations in the vapor space.

The following methods have been tried with varying success. None of these methods reduces filling losses materially:

LIGHT PAINT

Light-colored reflecting paints, such as aluminum, effect a substantial reduction in temperature variations in the vapor space. The resulting decrease in breathing loss more than compensates for the cost. Inasmuch as tanks must be painted for other reasons, the practice of using light-colored paints on tanks with gas-tight roofs with conservation vents has become almost universal.

WATER SEAL

A second method consists of carrying several inches of water on a flat steel roof of vapor-tight construction. This is accomplished by extending the top of the tank shell several inches above the roof. Although a great many roofs of this type were used at one time, they have come into disrepute, because the decrease is evaporation loss is hardly sufficient to compensate for the rapid deterioration of the roof plates caused by rusting.

WATER SPRAY

Temperature reductions may be achieved by means of a water-spray system. This method is considerably more efficient than the use of a water seal. Water is sprayed over the entire roof area by a series of nozzles; and, in some installations, is permitted to run down the tank shell. This increases the cost of tank maintenance, and the cost of operating the spray system is often not justified by the results obtained on products of average volatility.

INSULATION

Variations in temperature may be diminished by covering the roof with a layer of insulation. Evaporation tests indicate that a reduction in breathing loss of approximately 50 percent may be secured by the use of an efficient material. This method has not come into general use, because the initial cost of the insulation is rather high in comparison to the result secured.

SUNSHADES

Another method consists of the use of a metal hood, or sunshade, constructed of corrugated sheets of galvanized iron supported and held away from the tank

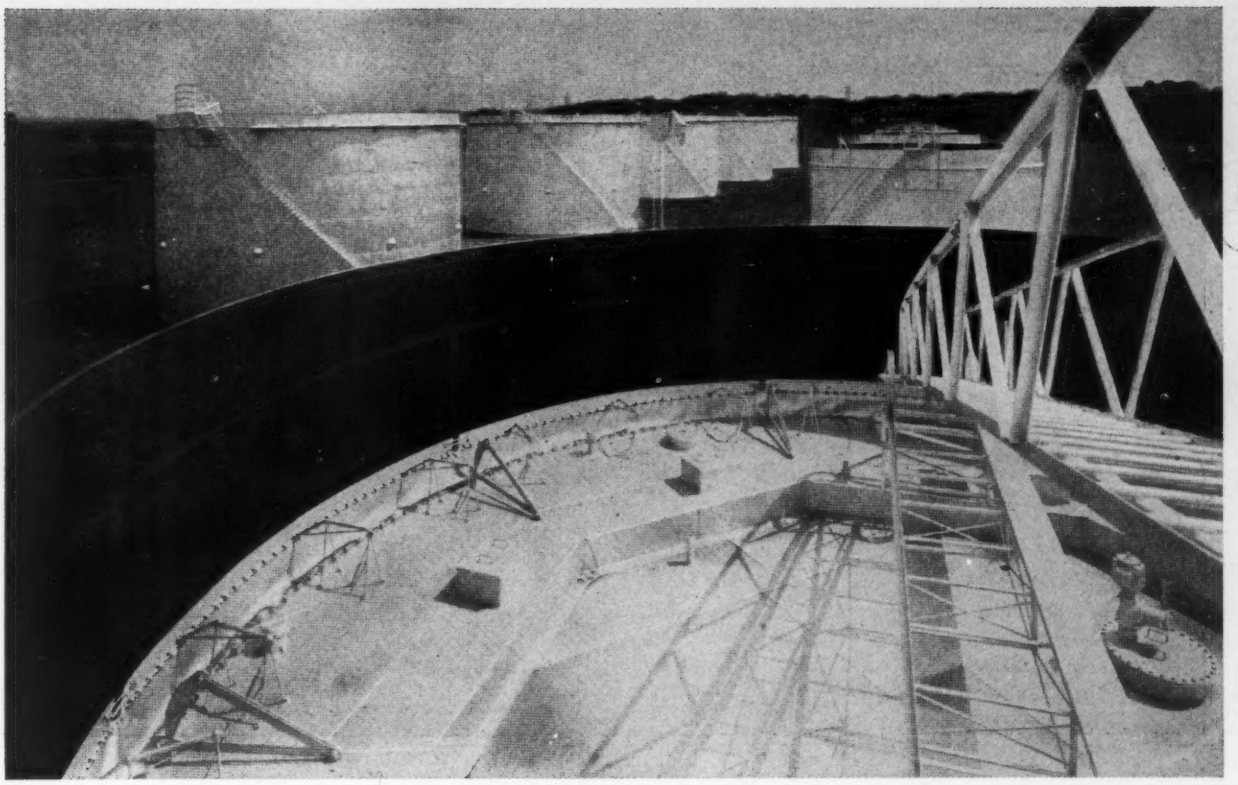


FIGURE 1
A Group of Welded Tanks with Wiggins Pontoon Roofs.

shell and roof by special framework of structural steel. Although such hoods effect some reduction in breathing loss, they have not been used extensively.

ELIMINATION OF VAPOR SPACE

Losses due to breathing, filling, and air circulation would not occur if a tank had no gas space above the liquid surface. It follows that such losses can be eliminated by providing a container whose volume can vary in such a way that a gas space never exists. This may be accomplished as follows:

WATER DISPLACEMENT

The vapor space in a tank can be excluded by introducing water to displace gasoline when it is withdrawn, and vice versa. Although this scheme has been popular with inventors, it has never appealed greatly to the oil companies, and has been used only in a few isolated cases.

FLOATING ROOF

A more practical way of doing away with the vapor space is to equip a cylindrical tank with a roof which floats on the oil surafce and rides up or down as the tank is filled or emptied. A floating roof prevents all filling loss, but permits a small standing loss, because a perfect method of sealing the space between the edge of the roof and the tank shell has not yet been devised.

The following types of floating roofs are in common use:

1. *Pan-type roof*: The first floating roofs consisted of a pan made up of a flat steel deck with a vertical rim at the edge. The space between the rim and the tank shell was closed by means of a special seal consisting of a series of steel shoes connected to each other by vertical strips of flexible material, and to the rim of the roof by a continuous strip of the same fabric. These roofs are effective in preventing evaporation loss from products not sufficiently volatile to boil at the temperatures attained by the steel deck plates. The pan-type roof may be used effectively for preventing evaporation losses from working crude-oil tanks, for resistance to corrosion in tanks containing sour crudes, and for fire prevention in any tank containing a volatile liquid.

2. *Pontoon roof*: The Wiggins pontoon roof consists of a single center deck plate attached at the periphery to a ring-shaped pontoon. The seal is similar to that used on the pan-type roof. The roof normally floats on the surface, thus eliminating breathing and filling losses in the same manner as a pan-type roof. However, it has several advantages not found in the latter. Vapor formed by boiling, instead of being lost, is trapped under the center deck and retained until re-absorbed by the liquid when cooler temperatures return. The pontoon roof is also more desirable from an operating standpoint; because it has much greater buoyancy, and is practically non-sinkable. The pontoon roof has met with greater favor than any of the older types of vapor-saving devices, and is particularly recommended for use on working tanks. A close-up view of a typical Wiggins pontoon roof in a butt-welded tank shell in shown in Figure 1.

VARIABLE VAPOR SPACE

Breathing losses can be stopped by constructing the tank roof in such a way that the vapor space can increase in volume when thermal expansion occurs, thus preventing vapor from being forced out of the tank and lost. The vapor thus retained again contracts, and is partly re-absorbed at the liquid surface when cooler temperatures return. The following types of roofs operate on this principle:

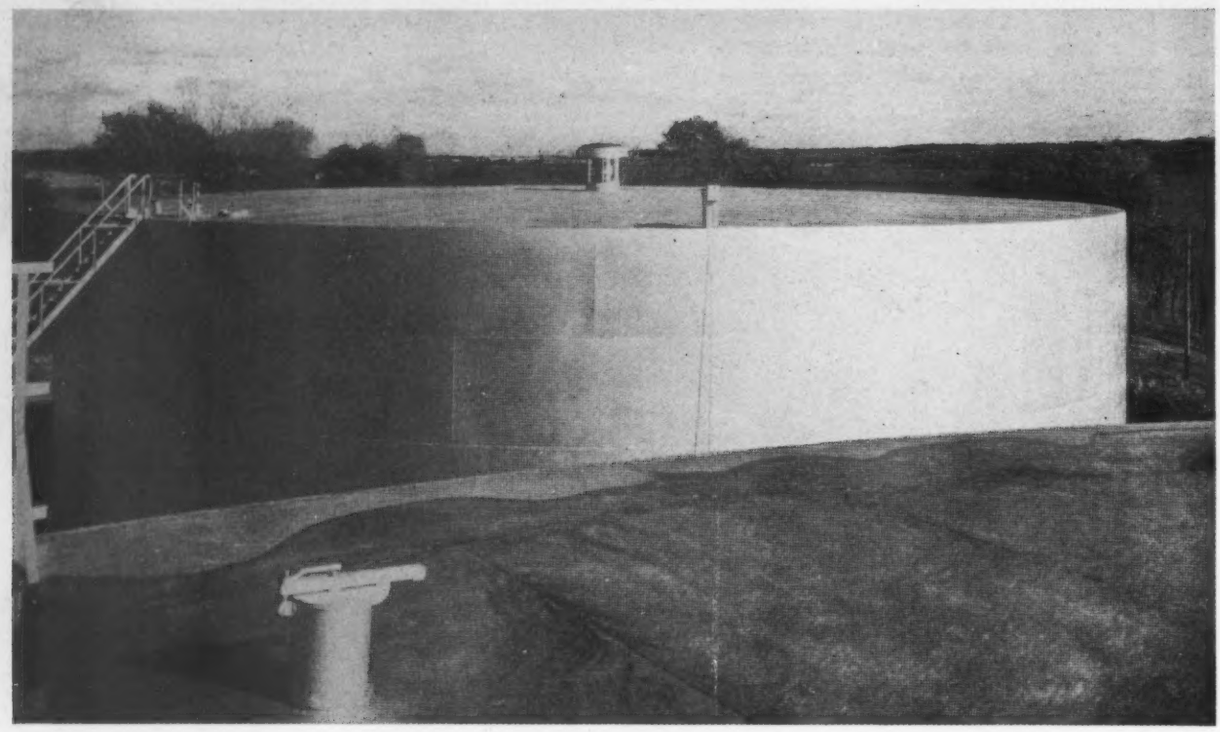


FIGURE 2
Wiggins Breather Roofs on Welded Tanks.

BREATHER ROOF

The breather roof is a flexible steel diaphragm covering the top of a storage tank. During periods when rising temperatures cause vapor expansion, the roof flexes upward to accommodate the increased volume. When decreasing temperatures cause the vapors to contract, the roof plates descend to a lower position. In this manner, all breathing loss is stopped. The Wiggins breather roof has sufficient capacity to prevent all standing loss from tanks filled or nearly filled with crude oil or motor gasoline. It was developed especially for this type of service, and is ordinarily used for storage tanks 60 feet or more in diameter. It does not prevent filling losses, and is not recommended for tanks worked rapidly. A Wiggins breather roof on a welded tank is shown in Figure 2, and a group of 144-foot diameter riveted API tanks with breather roofs is shown in Figure 3.

LIFTER ROOF

A lifter roof for an oil-storage tank operates in the same manner as a lift-type gasholder. It is commonly made up of a dome-shaped top with a depending rim which moves up or down in a trough containing a sealing liquid, usually water. When vapor expansions occur, the roof moves upward to provide the additional volume required. Although the lifter roof is very efficient in preventing evaporation losses, it has not been used as extensively as might be expected due, perhaps, to the high initial cost and the inconvenience of maintaining the seal in cold climates.

PRESSURE STORAGE

When a volatile product is stored in a container capable of withstanding the maximum vapor-space pressure normally attained, all venting is eliminated. Breathing and boiling losses are stopped completely, and filling losses are either reduced or eliminated—depending upon

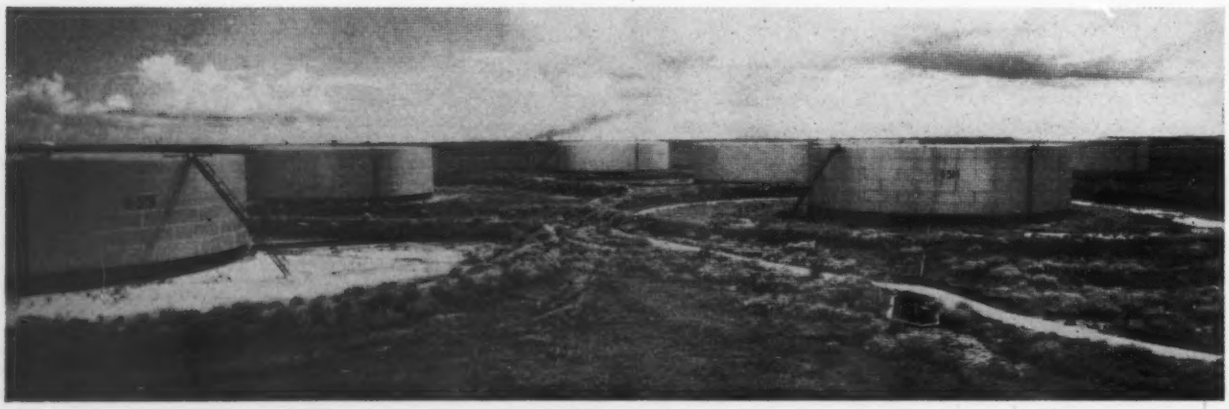


FIGURE 3
A Group of 144-Foot-Diameter Tanks with Breather Roofs.

vapor pressure of the stored product and the settings of the pressure and vacuum relief valves. In the past the following types of containers have been used for the storage of the more volatile hydrocarbons:

CYLINDRICAL VESSELS

Horizontal tanks consisting of a cylindrical shell with elliptical heads are used extensively for the storage of butane and propane for fuel purposes at industrial plants. Vertical blimps made up of a cylindrical shell with hemispherical heads at top and bottom are sometimes used for the storage of these materials at refineries. Such units have been built in capacities as high as 12,000 barrels.

SPHERES

The Hortonsphere is a spherical pressure vessel used for storing products ranging from the more volatile natural gasolines to butanes and propanes. Hortonspheres may be built in any capacity up to 20,000 barrels, and for pressures as high as 100 pounds per square inch, or more.

It is only within the last year or two that pressure storage has come into use for ordinary motor gasolines and the less volatile natural gasolines.

NEW DEVELOPMENTS IN STORAGE EQUIPMENT

A complete account of all recent developments in storage containers and their accessories would occupy more space than is here available. For this reason the discussion which follows has been limited principally to fundamental improvements in storage vessels.

FLOATING ROOFS

There have been no really outstanding developments in floating roofs since the Wiggins pontoon roof was introduced about eight years ago. Recent work directed toward increasing floating-roof efficiency has centered around improvements in the design of the seal, which closes the space between the rim of the roof and the tank shell. This seal is considerably more important than is generally realized. Even though the roof proper covers all but a small fraction of the entire tank area, excessive evaporation losses will occur if the liquid surface in the rim space is not effectively sealed.

EFFICIENCY OF THE WIGGINS SEAL

The seal on a Wiggins pontoon roof is made up of a series of steel shoes supported and held against the tank shell by hangers attached to the upper deck of the pontoon. Adjacent shoes are connected by vertical strips of fabric, and the tops of all shoes are connected to the deck by a continuous band of the same material—thus protecting the surface of the liquid between the shoes and the edge of the roof from the atmosphere, and preventing the circulation of air in this space. The only liquid which is ever exposed is that lying between the shoes and the tank shell. When the roof is passing over a horizontal seam, all of the shoes may be held a fraction of an inch away from the tank shell by the rivet heads—thus exposing a small surface at the bottom of a deep narrow aperture. Even so, the evaporation losses from this area are almost negligible during calm weather, because the vapor which forms at the surface tends to act as a blanket—thus retarding further vaporization. If a strong wind is blowing, however, some of the vapor may be carried out from behind the shoes, thereby increasing the rate of evaporation.

NEED FOR SECONDARY SEAL

The first Wiggins roofs were equipped with wiper seals to reduce the circulation of air between the shoes and the tank shell. These were soon abandoned, however, because a durable and resilient material for their construction could not be found. Furthermore, windage losses from the products of low volatility commonly stored at that time were not great enough to justify the expense involved in the installation of the additional seal. The vapor pressure of motor fuels has now been increased to the point where losses due to the circulation of air behind the shoes may be large enough to warrant the use of a secondary seal. This device has been re-designed using the improved materials now available.

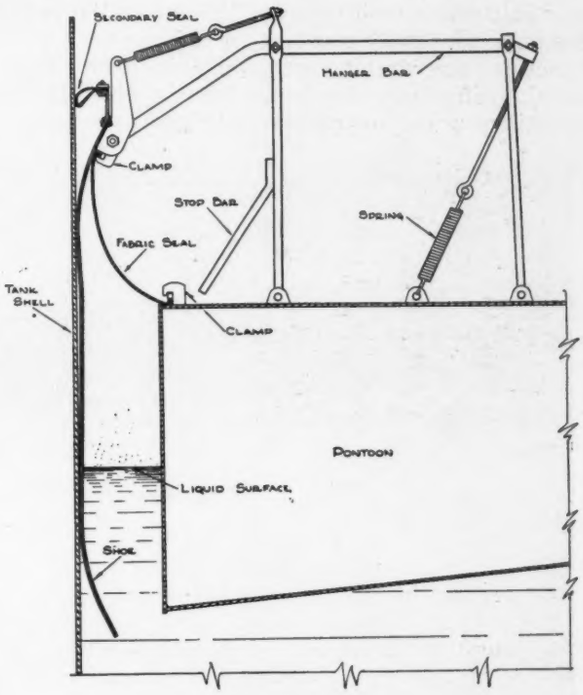


FIGURE 4
Secondary Seal for Wiggins Pontoon Roof.

The type of secondary seal recommended for floating roofs in riveted tanks in areas where prevailing winds are experienced is illustrated in Figure 4. It consists of a closed loop of a tough and resilient material mounted on an extension plate at the top of the shoe. This loop contacts the tank shell, and seals the space between it and the shoe. A secondary seal of this type has been in use for nearly two years on a 60-foot diameter riveted tank, which is filled and emptied once every day or two with sour distillate. It has given excellent results, and has proved sufficiently durable to be recommended for use on any floating roof in a territory where appreciable losses due to action of wind behind the shoes may be expected.

ADVANTAGES OF WELDED TANK SHELLS

Welded construction is now employed almost exclusively for all oil-storage tanks erected in the United States. The shell of a butt-welded tank can be built with a smooth inner surface having no obstructions of any sort. The shoes forming the seal of a floating roof fit such shells with piston-like precision—thus decreasing air circulation, and permitting the roof to operate at maximum efficiency.

When a floating roof is used in a riveted tank, the length of each shoe in a circumferential direction must be limited to about 3 feet to allow sufficient flexibility in passing over rivet heads and laps. A hanger must be provided for each shoe. When welded shells are used,

such limitations do not exist, and the length of each shoe may be increased from 3 to 40 or 50 feet. This eliminates a great many connections between shoes, and permits a wider spacing of hangers.

A typical seal with long shoes on a Wiggins pontoon roof in a butt-welded tank is shown in Figure 5. Other things being equal, butt-welded shells should always be specified for floating-roof tanks.

APPLICATION OF FLOATING ROOFS

Now that a number of efficient vapor-saving devices are commercially available, it is sometimes difficult to know just where each type can be used to the greatest advantage. Generally speaking, a floating roof should be used for any working tank containing motor fuel of normal boiling range, or for any tank in which fire protection is of prime importance. A Wiggins pontoon roof provides a sound investment for any tank filled or emptied more than five or six times per year with motor gasoline, or for any crude-oil tank filled oftener than once a month. The fire safety provided by a floating roof is too well known to merit further discussion here. Floating roofs may also be used to advantage in reducing losses from tanks used for blending purposes.

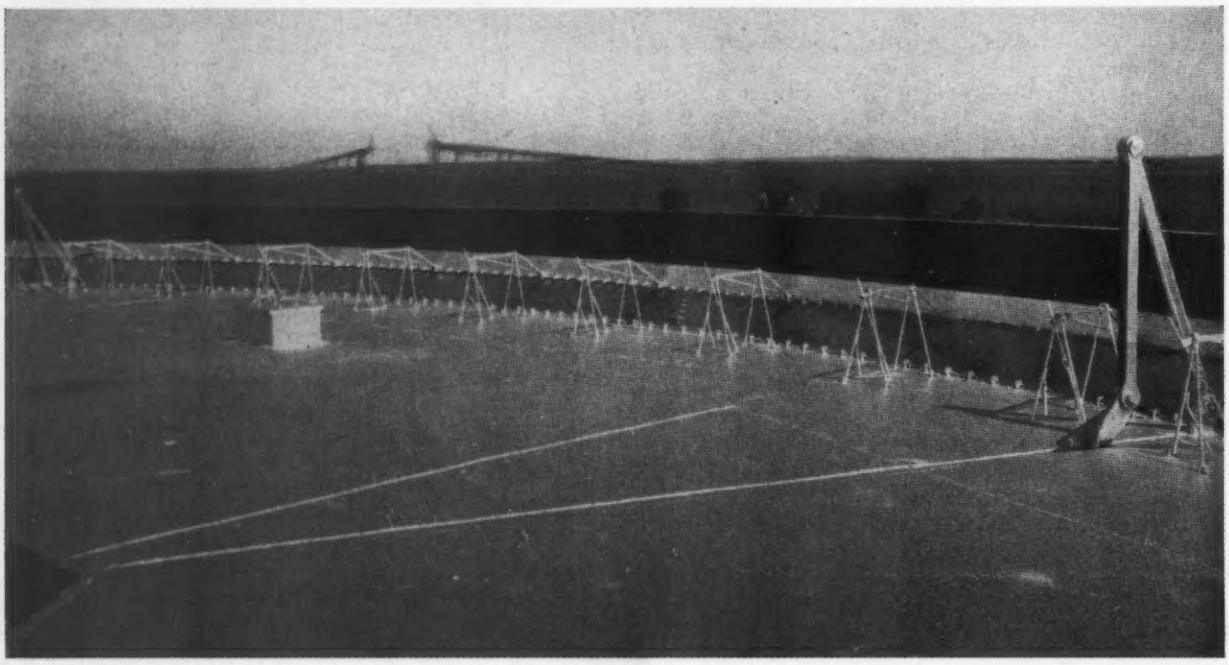


FIGURE 5
Wiggins Seal with Long Shoes in Welded Tank

BALLOON SYSTEMS

There are in use today thousands of structurally-sound cylindrical steel storage tanks with fixed roofs. The efficiency of many of these is being increased by removing the fixed roofs and replacing them with floating roofs or breather roofs. Such conversions are commendable from an economic standpoint, but are disrupting for the reason that the tanks must be taken out of service while the work is in progress. The search for a method of evaporation-loss prevention that could be applied to existing tanks without the necessity of taking them out of service culminated in the development of the Wiggins balloon system.

Vapor losses from a group of storage tanks with gas-tight steel roofs can be prevented by connecting the gas spaces through vapor lines to a suitable low-pressure gasholder. The vapors expelled from the tanks by pumping or breathing are forced through these lines to the gasholder, where they are retained temporarily. When the conditions causing their displacement have changed, the vapors pass back into the tanks, and are partly re-absorbed at the liquid surface. Inasmuch as most storage tank roofs are incapable of withstanding safely a pressure of more than 2 inches of water, the gasholder used in a system of this sort must be designed to operate at an unusually low pressure.

THE WIGGINS STEEL BALLOON

The Wiggins balloon is a gasholder having the distinguishing features of low operating pressure and relatively low cost. It provides a variable volume by the flexing of steel diaphragms, in much the same manner as a breather roof. A typical vapor-storage system employing a Wiggins steel balloon is shown at the top of Figure 6. The two sectional views at the bottom of Figure 6 show the outline of the balloon in the inflated and deflated positions. The upper part of the balloon consists of a large steel diaphragm attached to a vertical rim. This rim is fastened to another flexible plate extending outward from the top of a shallow tank shell with a flat bottom.

The top diaphragm of the balloon and the lower flexible extension are made of ⅛-inch steel plates with seams of single lap-welded construction. The rim, which is made of slightly heavier material, is reinforced at the top and bottom to resist the compressive stresses at these points. The bottom of the tank portion, which rests directly on the grade, may be constructed of ⅛-inch material—although a corrosion allowance of 1/16-inch is sometimes added.

VAPOR LINES

The vapor lines connecting the tanks and the balloon are made of light-gage pipe of large diameter in order to reduce friction loss and keep the cost to a minimum. Corrosion is minimized and painting facili-

tated by supporting the pipe above the ground on frames made of light angles. Inverted-siphon drains are placed at low points in the line to prevent an accumulation of water due to condensation.

OPERATION OF BALLOON

When all vapor has been discharged from the balloon, the diaphragm sags down and comes to rest on a series of fixed supports on the tank bottom, as shown in Figure 6. Incoming vapor causes it to lift off the supports and rise upward. Inasmuch as the diaphragm is constructed in the shape of a saucer, it cannot pass through the horizontal position without the formation of some buckles in the plates. A series of concrete weights placed on the deck along spiral lines helps to prevent local distortions by causing the buckles to form in long smooth waves. Spiral and circular control angles are also used as an additional safeguard against the formation of any sharp irregularities in the plates. The top weights and control angles on a 114-foot diameter balloon are shown clearly in Figure 7.

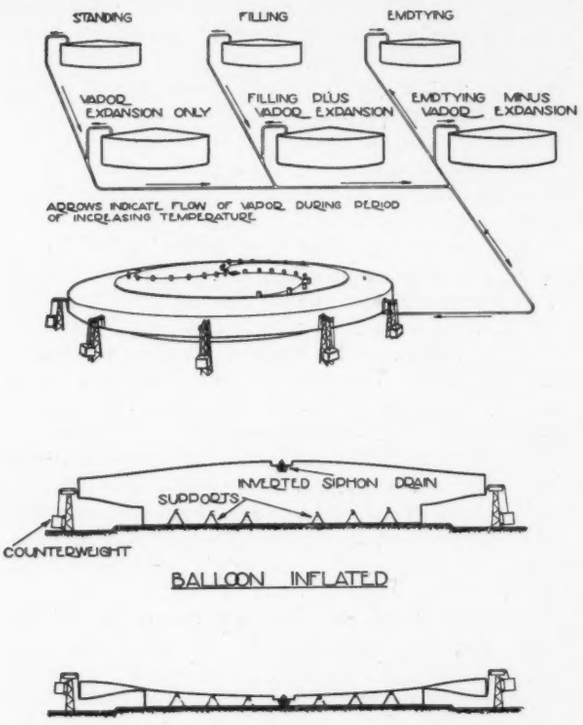


FIGURE 6
Wiggins Balloon System

As the diaphragm passes through the horizontal position and arches upward, it gradually lifts the rim by flexing the lower extension plate until the full capacity of the balloon is reached. The maximum operating pressure is held to a minimum by a series of counterweights which exert an upward force on the rim, and thus reduce the effort necessary to produce full inflation. The maximum operating pressure of a counterweighted balloon may be kept down to about 1⅝ inches or 1¾ inches of water. The counterweights consist of steel boxes filled with earth or gravel. They are suspended from cables or chains which pass over sheaves on steel posts and attach to the rim of the balloon.

The vents for a Wiggins balloon system consist of the usual pressure and vacuum vents on the tank roofs, supplemented by a special relief valve controlled by the movement of the balloon. Inasmuch as an almost unlimited amount of force is available to operate this valve when the balloon has reached its upper or lower limit, there is very little possibility of its failing to operate. All normal venting occurs through this valve. The tank-roof vents are set for slightly higher amounts of pressure and vacuum, and open only in an emergency. If

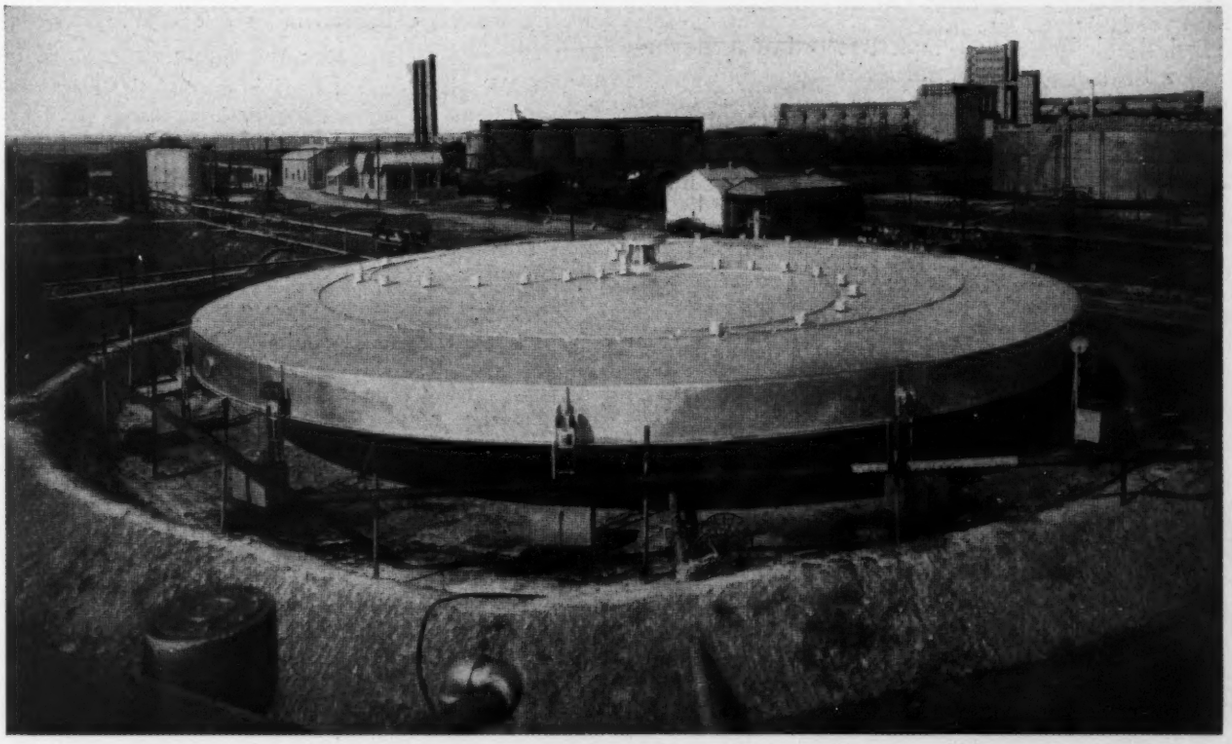


FIGURE 7
144-Foot-Diameter Wiggins Balloon Fully Inflated

a balloon with sufficient vapor-storage capacity has been chosen, there will be no venting from the system under ordinary service conditions.

A balloon system is entirely automatic in its operation. It will continue to function effectively as long as the fittings on all tanks are kept tightly closed. One good-sized opening in the system, however, may entirely destroy its efficiency in preventing evaporation losses. All tanks should be equipped with gage wells or automatic float gages, so that gaging may be accomplished without loss of vapor.

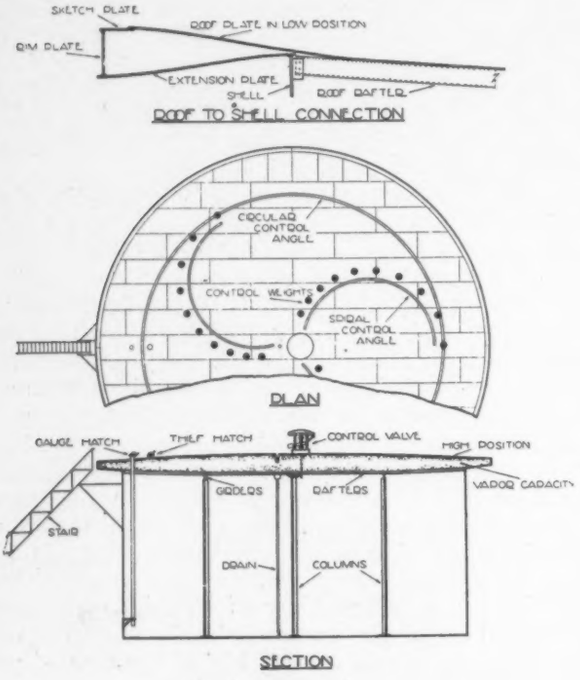


FIGURE 8
General Plan of Wiggins Balloon Roof

It is desirable to keep a complete record of the operation of a balloon system by installing an automatic recording gage to chart the movement of the balloon. The total volume of air and vapor returned from the balloon to the tanks each day can be determined from this chart. Then, if the percentage of hydrocarbon vapor in the mixture is known, the saving made by the system can be readily computed. This percentage can be obtained by making a daily analysis of the gas in the balloon with an Orsat apparatus to determine the oxygen content. This indicates the percentage of air in the mixture, and the remainder is hydrocarbon vapor.

TABLE 1
Balloon-Roof Data

Tank Diameter (Feet)	Roof Diameter (Feet)	Vapor Capacity (Cubic Feet)	Rim Height (Inches)	Maximum Pressure (Inches of Water)
20	32	1,300	13	6⅞
30	42	2,400	13¼	6⅝
40	52	4,300	13½	5⅞
50	62	6,800	14⅜	5⅜
60	72	10,200	15¼	5
70	82	14,500	16⅛	4⅝
80	92	20,000	17	4¼
90	102	27,000	17⅞	4
100	112	35,000	18¾	3¾
110	122	44,000	19⅛	3½
120	132	55,000	19½	3¼
130	142	67,000	19⅝	3⅛
140	152	79,000	19¾	3
150	162	91,000	19⅞	2⅞
160	172	103,000	20	2⅞

APPLICATION OF WIGGINS BALLOON SYSTEM

A Wiggins balloon system may be installed wherever sufficient ground space for its construction is available adjacent to a group of storage tanks with gas-tight steel roofs. It should not be thought, however, that the balloon system is a panacea for any group of tanks that happens to be suffering extreme evaporation losses. A careful investigation of the proposed installation should be made to see whether it is practical and can be expected to function efficiently. The roofs on all tanks to be included in the system should be examined to determine whether the seams and fittings are gas-tight, or whether they can be made so at a reasonably small cost. Special attention should be given to fittings such as old-style foamite boxes, which are rarely gas-tight and are difficult to repair.

The design of each roof should be checked to make sure that the top angle has the strength necessary to resist the compressive stress due to pressure. When necessary, the stress at the curb can be either reduced or eliminated entirely by placing weights on the roof to decrease the net upward force due to pressure. This can usually be done without overloading the roofs; because the supporting columns are ordinarily selected on the basis of slenderness ratio, and are capable of supporting greater loads than those contemplated in the design. A cone roof, which has been equipped with weights to increase the safe operating pressure, may be seen in the background at the right of the balloon in Figure 7.

Each proposed balloon system presents an individual problem requiring careful study. All pertinent factors such as relative positions and elevations of the various tanks, condition of roofs and fittings, vapor pressures of products stored, pumping rates, and throughputs must be considered in arriving at the most economical capacity for the balloon and for the proper diameters for the various vapor-line branches. An installation based on a study of this sort will operate satisfactorily, and will make a good return on the investment, if reasonable care is exercised in its operation.

BALLOON ROOFS

The Wiggins balloon roof is one of the most recent developments in vapor-saving devices. It looks and operates like a steel balloon mounted on the top of a storage tank, and derives its name from this resemblance. The principal difference between the steel balloon and a balloon roof is that counterweights are seldom used with the latter for the purpose of reducing the operating pressure.

FEATURES OF WIGGINS BALLOON ROOF

The component parts of a Wiggins balloon roof are illustrated by the general plan in Figure 8. When the roof is deflated, the top deck or diaphragm rests on a framing of rafters and girders supported on columns. A system of top weights and control angles, similar to that used on a steel balloon, is installed on the top to make the buckles form in smooth waves as the deck passes through the horizontal position.

Most balloon roofs have been constructed with an overhang, or extension, beyond the tank shell of 6 feet—thus making the roof diameter 12 feet greater than the diameter of the tank. Increased roof capacity can be secured by extending this dimension. A few roofs have been built with an 8-foot overhang. The maximum operating pressures, rim heights, and net vapor-storage capacities for roofs of various diameters with 6-foot overhang and 3/16-inch roof plates are listed in Table 1. The operating pressure of a balloon roof varies in-

versely with the diameter. It is considerably greater than the pressure for a steel balloon of the same size. This is true because heavier plates are used in the construction of a balloon roof, and because counterweights for reducing the pressure are not used except in special cases. A typical balloon roof with 6-foot overhang is shown in Figure 9.

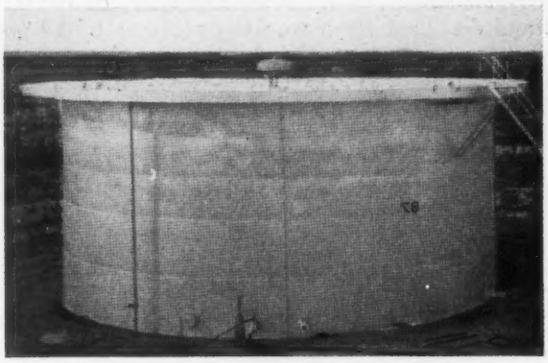


FIGURE 9
85-Foot-Diameter Balloon Roof on 73-Foot Tank

The fittings normally supplied with a Wiggins balloon roof consist of a thief hatch, gage hatch, manometer drainage system, and control valve for venting the roof when its capacity tends to be exceeded. The gage hatch is equipped with a well extending down into the liquid to prevent loss of vapor during gaging. The drain consists of an inverted siphon located at the center of the deck. Water passing through this drain overflows into a catch basin, and is conducted to the tank bottom through a vertical pipe which prevents it from coming into contact with the main body of the stored liquid as it descends. After it has reached the tank bottom, the water may be removed through the regular water drawoff. In cases where it is undesirable to permit rain water to enter the tank, a pipe-drainage system with flexible joints may be used to carry the water from the deck to the outside of the tank shell.

VENTING MECHANISM

No vapor-saving device can be expected to operate at full efficiency unless it is equipped with pressure and vacuum relief vents which open without fail when the need for venting exists, and remain tightly closed at all other times. The double-acting diaphragm control valve illustrated in Figure 10 was developed to provide breather and balloon roofs with a venting device that would fulfill these requirements, even under the most severe climatic conditions. The operation of this mechanism is as follows:

1. *Vacuum*: When a partial vacuum forms in the tank, the valve cover is forced downward by atmospheric pressure—thus causing the valve to open as shown in Figure 10. The amount of vacuum at which the valve starts to open can be regulated by varying the amount of weight in the counterweight box.

2. *Pressure*: When vapor tends to be displaced from the tank during filling or as a result of thermal expansion, the pressure gradually increases—causing the roof to inflate. As it reaches the high position, the stop block contacts the rafters, and the valve will then open with any further upward movement of the roof plates.

The dome-shaped cover has a diameter of 5 ft. 6 in., and its large effective area provides ample force to open the valve even when it is frozen shut with film of ice. This has been verified by actual test. When the roof has become partly inflated, but has not reached the position where the stop block touches the rafters, the pressure inside the vent cover tends to force it upward —thus closing the valve so tightly that no leakage can possibly occur. The first valves of this type were installed about 2½ years ago, and their service record has been remarkably good.

INTERCONNECTION WITH FIXED-ROOF TANKS

When a tank with a balloon roof is to be connected by vapor lines to one or more adjacent tanks with fixed roofs, the design and condition of the fixed roofs must be investigated to make sure that they will withstand safely the maximum operating pressure. If the roofs are found to be inadequate, the pressure requirements may be handled in one of the following ways:

1. The fixed roofs may be reinforced by adding section to the top angle to reduce the unit compressive stress due to pressure. This method is often impractical, because it necessitates taking the roofs out of service to permit welding.

2. Concrete weights can be placed on the fixed roofs to reduce the net upward pressure acting on the roof plates, thus decreasing or eliminating the compressive stress at the curb. The framing on most cone roofs has

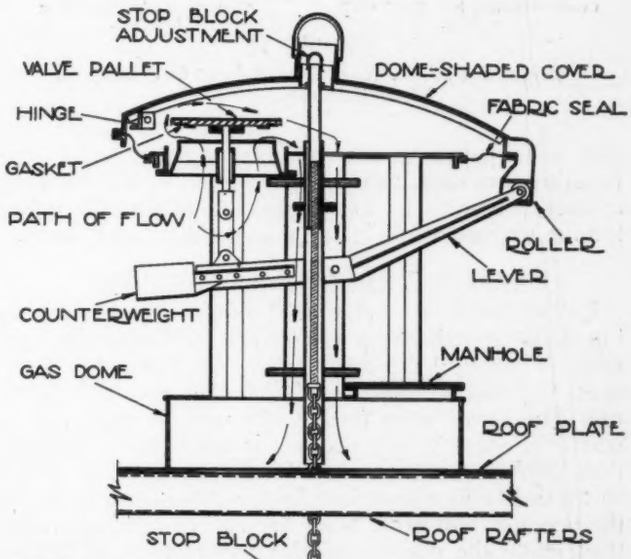

STOP BLOCK ADJUSTMENT
VALVE PALLET
DOME-SHAPED COVER
FABRIC SEAL
HINGE
GASKET
PATH OF FLOW
ROLLER LEVER
COUNTERWEIGHT
MANHOLE
GAS DOME
ROOF PLATE
STOP BLOCK
ROOF RAFTERS
NOTE: WHEN A PARTIAL VACUUM FORMS IN THE TANK, THE COVER IS FORCED DOWN BY ATMOSPHERIC PRESSURE, CAUSING THE VALVE TO OPEN AS SHOWN ABOVE. AS PRESSURE BUILDS UP IN THE TANK, THE ROOF RISES UNTIL THE STOP BLOCK ENGAGES THE RAFTERS, AND FURTHER MOVEMENT OF THE ROOF OPENS THE VALVE. THE PATH OF FLOW THROUGH THE VALVE IS THEN THE REVERSE OF THAT SHOWN ABOVE.

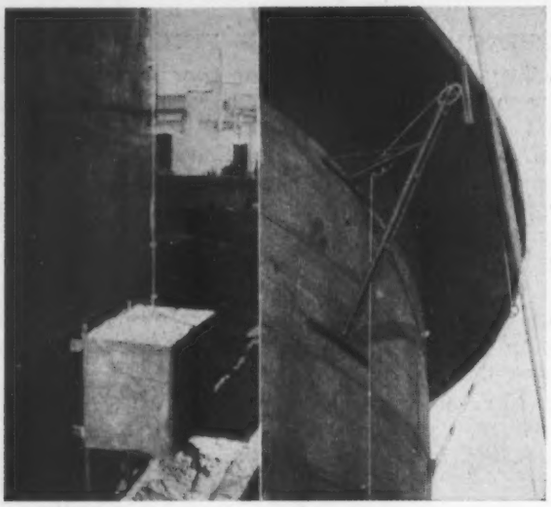
FIGURE 10
Diagram Showing Operation of Volume Control Valve

the strength necessary to support these weights in addition to the usual roof loads, provided they are placed directly over the columns.

3. The overhanging portion of the balloon roof may be counterweighted to reduce the maximum operating pressure. This is accomplished by exerting an upward force on the rim by means of weights suspended on cables passing over sheaves mounted on brackets attached to the tank shell. This arrangement is illustrated

by the views in Figure 11, which were taken during the erection of a 76-foot-diameter balloon roof on a 60-foot tank. The gin pole used for raising the roof plates may be seen at the left of the left-hand photograph.

Fixed roofs on new tanks which are to be connected through vapor lines to a balloon roof should be designed for the maximum pressure to which the system may be subjected, and should be equipped with fittings



Counterweight box filled with gravel. Sheaves and supporting bracket.

FIGURE 11

Wiggins Balloon Roof with 8-Foot Overhang on 60-Foot-Diameter Tank.

that will operate at this pressure without vapor loss. Existing tanks can usually be modified to withstand increased pressures by using concrete weights to reduce the net upward force in the manner described above.

APPLICATION OF BALLOON ROOF

Balloon roofs are being used extensively for marketing tanks at bulk stations and marine terminals. Such stations usually have one or more small tanks used for special grades of motor fuels handled in small quantities. The losses from these tanks may be quite serious when the value of the product is taken into consideration. Unfortunately, a special roof for a small tank is so expensive in comparison to the cost of the tank that the operator will often allow the loss to continue rather than make the outlay necessary to stop it. A balloon roof with some excess capacity installed on one of the larger tanks at the terminal offers a convenient solution of this problem. Vapor lines extended to the small tanks will prevent all breathing loss, and will effect some reduction in filling loss at a relatively small cost.

HORTONSPHEROIDS—PRESSURE STORAGE

Although engineers in the petroleum industry have been familiar with the advantages offered by pressure storage, the use of pressure vessels for the storage of large volumes of motor fuels at the low pressures required to prevent evaporation loss is a comparatively recent development. One of the first applications of the pressure-storage principle consisted of the use of small cylindrical vessels with elliptical heads for butanes and other light fractions requiring relatively high pressures. This was followed by the introduction of spherical vessels which provided more economical storage where fairly large quantities were involved. The first Hortonspheres had riveted seams, but welded construction has been employed almost exclusively during recent years. Two typical welded Hortonspheres, designed for a working pressure of 100 pounds per square inch and used for the storage of butane, are shown in Figure 12. These vessels have a diameter of 35 feet 3 inches and a capacity of 4,000 barrels each.

The Hortonspheroid was introduced to the oil industry on a commercial scale in 1929. During that year four riveted units, each having a capacity of 10,000 barrels and designed for a working pressure of 15 pounds per square inch, were placed in service for the storage of natural gasoline. A riveted spheroid of this capacity and pressure is illustrated in Figure 13. A welded unit

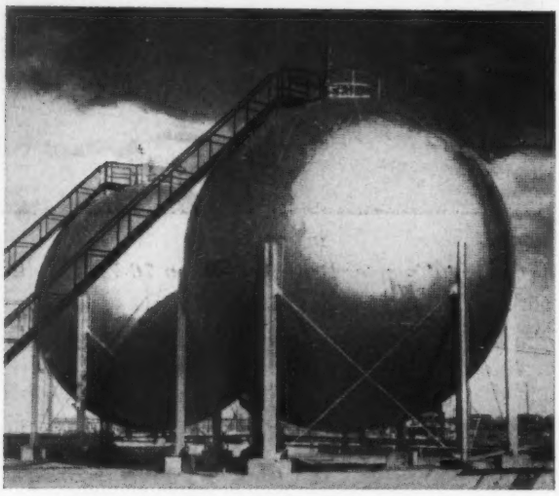


FIGURE 12

Two 4,000-Barrel Welded Hortonspheres

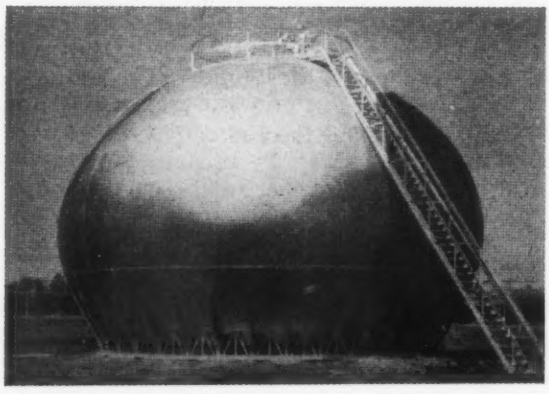


FIGURE 13

10,000-Barrel 15-Pound Riveted Hortonspheroid

of the same size with spiral stairway is shown in Figure 14.

THE HORTONSPHEROID PRINCIPLE

The distinguishing feature of the Hortonspheroid is its characteristic streamlined contour. The fundamental principle involved in the choice of this particular shape may be explained as follows: When any elastic container such as a rubber bag is filled with liquid and then subjected to internal gas pressure, it takes the shape for which the shell stresses are uniform and minimum. The weight of the liquid tends to flatten the bag, while the gas pressure tends to inflate it. The resulting shape is known as a spheroid. The exact curve assumed by the shell depends upon the weight of the liquid and the magnitude of the gas pressure.

The Hortonspheroid, as originally conceived, consisted of a steel shell built to the shape which an elas-

tic container would take when filled with liquid of the weight to be stored and subjected to the specified working pressure. This form is the one requiring the least amount of steel. An outside girder was provided to support the weight of the liquid in the overhanging portion of the shell at times when no gas pressure existed, but no framing or bracing of any sort was used inside the vessel. Spheroids of this type having

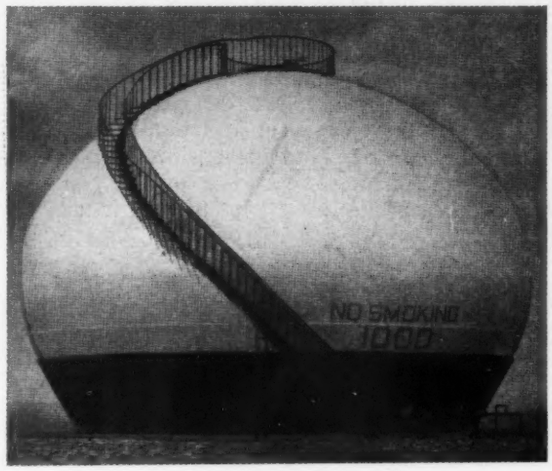
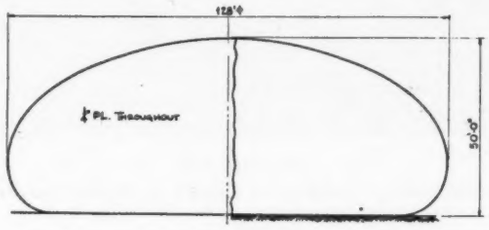


FIGURE 14
10,000-Barrel 15-Pound Welded Hortonspheroid

no internal framing are now usually called "plain" or "smooth" spheroids, to differentiate them from the noded type of spheroid with inside trusses and ties which was developed later. Plain spheroids have been built in capacities up to 30,000 barrels, and for working pressures as high as 25 pounds per square inch.

DEMAND FOR PRESSURE STORAGE

The increasing use of spheroids for volatile products tended to emphasize the inherent simplicity and natural advantages of pressure storage. This, in time, resulted in a demand for a pressure container that could be built



Capacity, 80,000 barrels
Working pressure, 2½ pounds per square inch

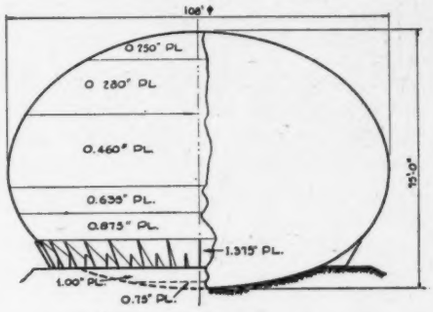
FIGURE 15
Ideal Hortonspheroid

in any capacity up to 100,000 barrels, and used for motor gasolines and natural gasolines necessitating working pressures ranging from 2½ to 15 pounds per square inch, or more. Attempts to design a vessel which would meet these requirements and could be sold at a reasonably low price led to the development of the noded type of Hortonspheroid.

LIMITATIONS OF IDEAL SHAPE

In order to understand the factors involved in providing storage facilities for large quantities of liquid at low pressures, let us consider the problem of designing a container for storing 80,000 barrels of gasoline weighing 48 pounds per cubic foot at a maximum working pressure of 2½ pounds per square inch. An elastic shell or bag filled with this amount of 48-pound liquid and subjected to a 2½-pound pressure would take the shape shown in Figure 15, which we shall call the "ideal" shape. The stress in any direction at any point in the shell would be 2500 pounds per lineal inch. If the vessel were to be subjected only to this particular combination of gas and liquid loads, the entire shell —including roof and bottom—could be constructed of ¼-inch steel plates.

Unfortunately, a pressure tank in service may be subjected to all possible combinations of liquid and gas loads, and the shell must be designed for the maximum stresses resulting from any combination. If gas pressure alone were applied to the vessel illustrated in Figure 15, it would tend to assume a spherical shape—resulting in high compressive stresses in the lower part of the shell where the radius of curvature is sharpest. Liquid load unaccompanied by gas pressure would cause excessively-high tensile stresses in the same region. These considerations make it necessary to abandon our "ideal" shape and adopt one that is better suited to actual conditions.



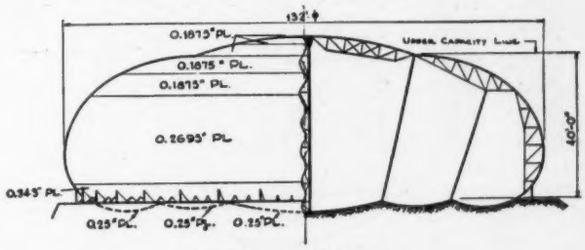
Capacity, 80,000 barrels
Working pressure, 2½ pounds per square inch

FIGURE 16
Smooth Hortonspheroid

LIMITATIONS OF SMOOTH SPHEROID

The high compressive stresses in the shell of the "ideal" spheroid can be reduced or eliminated completely by changing the radii of curvature. The flat bottom can be made to withstand gas pressure by dishing it. The high tensile stresses due to liquid alone can be resisted by increasing the plate thickness and providing a girder to support the overhanging portion of the shell. These modifications result in the typical smooth spheroid, shown in Figure 16. It has a diameter of 108 feet and an over-all height of 75 feet. Although a vessel of this design is structurally sound and capable of resisting all combinations of loads, it has a number of undesirable features—some of which are:

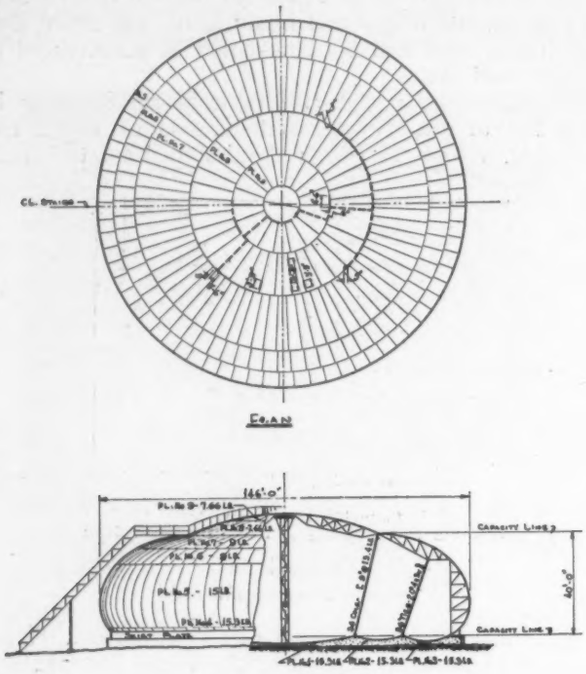
1. The height causes a soil pressure too great to permit the use of the vessel in many locations. 2. The



Capacity, 80,000 barrels
Working pressure, 2½ pounds per square inch

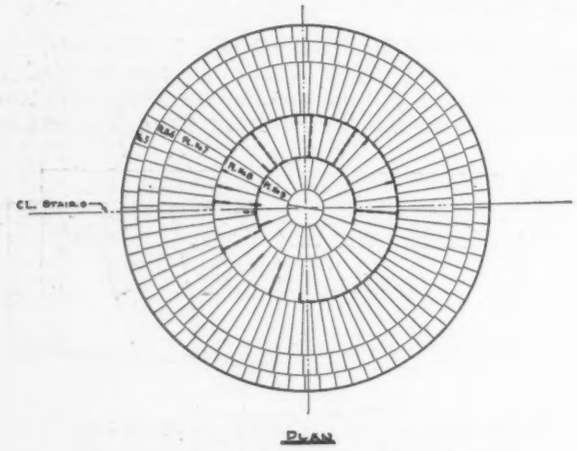
FIGURE 17
Noded Hortonspheroid

welding of the heavy plates in the lower shell might cause locked-up stresses if an improper welding sequence were used. 3. The high cost of fabricating and erecting the heavy plate work is reflected in the selling price of the vessel.



Working pressure, 2½ pounds per square inch
Breaking pressure, 6 pounds per square inch
First test, January 22, 1938.
40 feet of water in tank when tested
NOTE: Heavy dotted lines indicate fractures

FIGURE 18
First Failure Test, 100,000-Barrel Hortonspheroid



Working pressure, 2½ pounds per square inch
Breaking pressure, 5.3 pounds per square inch
Second test, March 18, 1938
32.8 feet of water in tank when tested
NOTE: Heavy dotted lines indicate fractures

FIGURE 19
Second Failure Test, 100,000-Barrel Hortonspheroid

From the foregoing, it is evident that the smooth spheroid, which is admirably suited to the storage of volumes up to 30,000 barrels at high pressures, is not so well adapted to the storage of larger volumes at low pressures.

DEVELOPMENT OF NODED HORTONSPHEROID

All of the objections to the use of the smooth spheroid for large-volume low-pressure storage can be overcome by further modifications in the design. The excessive height can be reduced by flattening the structure and introducing internal tension members to preserve the flattened shape under gas pressure. The shell plates can be reduced in thickness by the use of trusses designed to effect a more uniform distribution of stresses under liquid load. A noded-type Hortonspheroid having these features is shown in Figure 17.

The stress formulas used in the design of noded Hortonspheroids have been developed through analytical research and field stress measurements. In general, the basic principles of design consist of forming all plates to a double curvature to increase their efficiency in resisting pressure, and in placing all structural members to act both as tension members and as compression members—depending on the conditions of loading. All of the metal in the structure is thus utilized at maximum efficiency.

EFFECT OF EXCESSIVE GAS PRESSURE

The purchaser of a Hortonspheroid is naturally interested in knowing how it would fail as a result of excessive gas pressure caused either by an explosion or by the failure of the relief vents to function. A rational analysis of this problem indicates that the roof plates will rupture without damage to the rest of the structure. The major portion of the total stress in the outer shell is caused by liquid. The gas stress in this

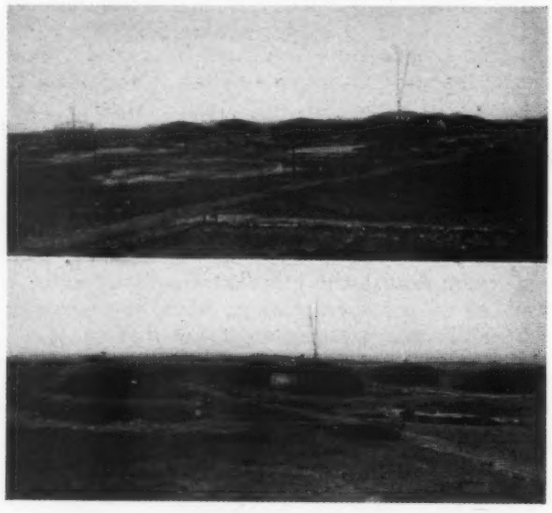


FIGURE 20
Construction Views of a Group of 100,000-Barrel 2½-Pound Hortonspheroids.

region is comparatively small. Increasing the gas pressure above the working range will cause a relatively small increase in the total shell stress. The roof plates, however, are stressed in direct proportion to the gas pressure, and will fail long before a critical stress has been reached in the shell.

FAILURE TEST OF 100,000-BARREL SPHEROID

In order to verify the theory outlined in the preceding paragraph, a 100,000-barrel spheroid designed for a working pressure of 2½ pounds per square inch was tested to failure by applying excess gas pressure. It was first filled with water to the top capacity line. The pressure in the vapor space was then increased by introducing compressed air until failure occurred, at a pressure of 6 pounds per square inch, by the tearing of the single lap-welded seams in the roof. The seams along which tearing occurred are indicated by the heavy dotted lines in the plan view shown in Figure 18.

After this test had been completed, the roof was re-

paired and again tested to failure under different conditions. During the second test the spheroid was filled with water to a depth of only 32.8 feet, instead of 40 feet, as in the first test. The second failure occurred with greater violence than the first due to the larger volume of compressed air in the vessel. The roof seams which tore during the second test are indicated on the plan view in Figure 19. Some parts of the roof were thrown entirely clear of the spheroid. The data gained

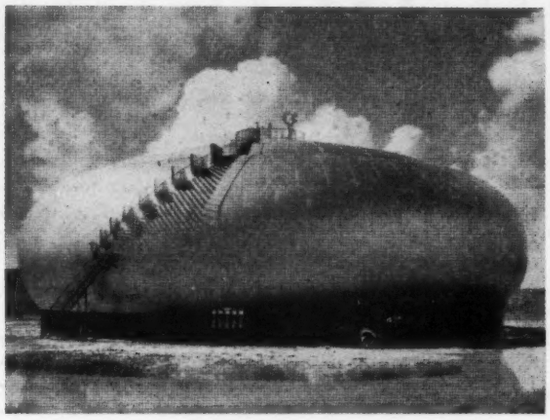


FIGURE 21
100,000-Barrel 15-Pound Hortonspheroid

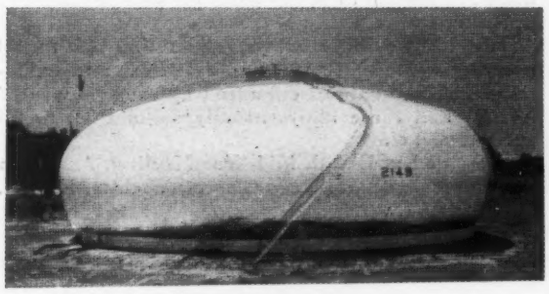


FIGURE 22
100,000-Barrel 15-Pound Hortonspheroid

from these tests furnish conclusive proof that the roof of a Hortonspheroid provides a so-called weak section for the relief of excessive pressure. The conditions to be dealt with in a spheroid fire following an explosion would be similar to those encountered with cylindrical storage tanks. Of course, the rich vapor mixture normally present in a pressure vessel is excellent insurance against the occurrence of such an explosion.

ADVANTAGES OF PRESSURE STORAGE

A few of the desirable features obtained through the use of pressure storage are as follows:

1. *Positive protection*: When volatile products are stored in closed containers whose relief vents are set to open only when the pressure necessary to prevent breathing has been reached, there can be no question that the desired result has been accomplished. As long as venting does not occur, there can be no vapor loss and no accompanying deterioration of product.

2. *Dependability*: A pressure vessel has the fewest working parts of any of the generally-accepted evaporation saving devices. Aside from the pressure and vacuum relief valves, there is nothing to get out of order. A vessel of this type is necessarily a rigid structure which is unaffected by rain, snow, or ice.

3. *Low maintenance cost*: Pressure containers prevent evaporation losses by taking advantage of the very physical laws responsible for this occurrence. No power is used, and the presence of an attendant is not required. There are no special maintenance costs of any sort.

4. *Corrosion resistance*: When a pressure vessel has been in service long enough for the vapor mixture in the gas space to reach a state of equilibrium, air will be drawn in through the relief vents only under unusual operating conditions. Inasmuch as oxygen is one of the principal factors responsible for a high rate of corrosion, the exclusion of air helps materially to increase the useful life of the structure.

5 *Fire safety*: The rich vapor mixture present in a pressure vessel also helps to minimize the fire hazard. The vapor content of the gas space is always above the explosive range under normal operating conditions.

FIELD FOR PRESSURE STORAGE

The development of the noded type of Hortonspheroid has made pressure storage economically available for a wide range of volatile products. Typical spheroid installations are illustrated in Figure 20, 21, and 22. The views in Figure 20 show a large group of low-pressure Hortonspheroids in the process of construction. Each one has a capacity of 100,000 barrels, and is designed for a working pressure of 2½ pounds per square inch. Figure 21 shows a 100,000-barrel 15-

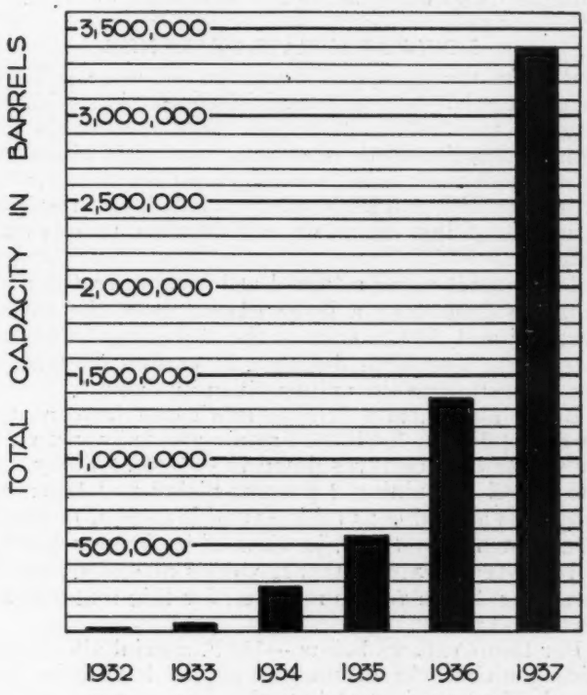


FIGURE 23
Graph Showing Total Capacities of Hortonspheroids Placed in Service Each Year.

pound vessel used for storing natural gasoline. A 100,000-barrel 10-pound unit may be seen in the background. Another 100,000-barrel 15-pound spheroid used for natural-gasoline storage is shown in Figure 22. The rapidly-increasing use of this class of storage is indicated by the chart in Figure 23, which shows the number of barrels of Hortonspheroid storage purchased each year by the oil industry since 1932. The desirable features of simplicity, safety, and economy offered by pressure storage point to further marked increases in the use of Hortonspheroids for all classes of volatile liquids, particularly those which must be protected against loss in quality as well as evaporation.

Nickel-Bearing Alloys *Used in* Petroleum Refining

B. B. MORTON
The International Nickel Company, Inc.
New York

NICKEL-BEARING alloys are widely used in refineries to meet the strenuous demands imposed on metals by the wide variations of temperature (— 150 to 2,000° F.) used and the presence of organic and mineral corrosive agents.

The 2.25 percent nickel steels readily meet the requirements for vessels and equipment operating at the sub-zero temperatures used during dewaxing of lubricating oils. Monel, nickel, Inconel, and the 18-8 alloys are available for use where very low temperatures are encountered; and offer the optimum in strength, ductility, and impact resistance.

Ni-Resist, an austenitic cast iron, is one of the most widely used of the nickel-bearing alloys, and finds application as pump parts for pumps handling naphtha, reflux, acids, and bases.

The heat-resisting alloys, containing 25 to 30 percent chromium, have their physical and oxidation-resisting qualities enhanced by the presence of nickel; and these alloys usually contain 12 to 25 percent nickel.

Presented at Eighth Mid-Year Meeting, American Petroleum Institute, Lassen Hotel, Wichita, Kansas, May 25, 1938.

PETROLEUM refiners, especially with their newly-acquired flair for production of chemicals, make strenuous demands upon metals and alloys. Metal temperatures ranging from —150°F. and lower to about 2000°F. are encountered at various locations in refineries. The presence of sulfur, also organic and mineral acids, further intensifies the service requirements by introducing the factor of corrosion.

LOW-TEMPERATURE RANGE

Within the temperature range of 0 to —75°F., encountered by metals used in connection with dewaxing, the 2.25 to 2.50 percent nickel steels find wide application as the material for vessels, pipes, and fittings. This material is well suited for the service; as it is readily available, easily welded, and retains a satisfactory impact value within this temperature range.

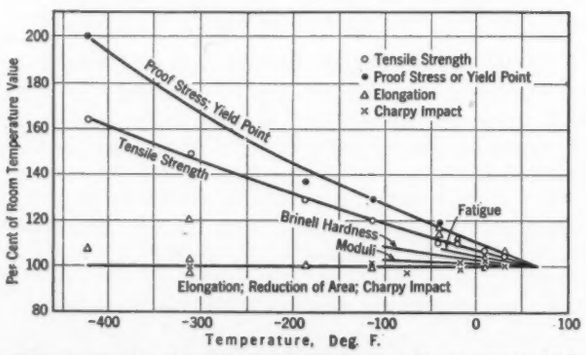
The impact value retained at low temperatures appears to depend to a large extent upon the carbon content; and, in the case of the nickel steels, impact values improve with decrease in carbon content, as can be seen from the values given in Table 1.

Bolts, piping, and fittings fabricated from a steel corresponding to SAE 2315 retain ample impact value for use at temperatures down to —75°F. "Yoloy," an alloy steel containing 2 percent nickel and 1 percent copper, is available as tubing; and is used at temperatures down to —75°F., in view of its large retention of room-temperature impact values at sub-zero temperatures. Some values reported for this material are given in Table 2.

For temperatures below —75°F. special alloys containing nickel, chromium, and copper have been proposed. The very low carbon-nickel irons possess good impact values at temperatures down to —200°F. (see Table 1). However, for the ultimate in strength, ductility, and impact values, Monel, nickel, and Inconel, also the 18 percent chromium-8 percent nickel stainless steels, are available. Table 3 gives some impact values for Monel, nickel, and Inconel; and Figure 1 presents curves showing the effect of sub-zero temperatures on the physical properties of Monel. From these curves it is evident that the impact value of Monel does not drop off at temperatures down to —425°F.; the physical strength improves; and the ductility, as measured by elongation and reduction of area, remains fairly constant. Monel is in use at the present time as the bowls of centrifuge machines used in connection with dewaxing of lubricating oil. It also finds service as bolts and as a material for highly-stressed parts. Its resistance to corrosion by chlorinated solvents further enhances its value when used in connection with dewaxing in the presence of these solvents.

The 18 percent chromium-8 percent nickel alloys are reported to possess excellent physical properties and impact values at temperatures down to that of boiling liquid air.

Cast nickel steels are widely used in connection



Ultimate tensile strength, 70,000-85,000 pounds per square inch.
Yield point, 30,000-40,000 pounds per square inch.
Elongation in 2 inches, 50-35 percent.
Reduction of area, 75-65 percent.
Brinell hardness number, 120-160.
Izod impact value, 120-90 foot-pounds.
Charpy impact value (45° notch), 215 foot-pounds.

FIGURE 1
Effects of Sub-Zero Temperatures on the Physical Properties of Monel.

Mr. Morton, graduated from high school in Pulaski, Va., in 1916, served with the Virginia National Guard on the Mexican border. During the World War he was commissioned Second Lieutenant while in France, and also served with the Army of Occupation. In 1921, he entered Virginia Polytechnic Institute and majored in metallurgy. After graduation, he served in Mexico with American Smelting and Refining Company; at Lackawanna, N. Y., with Bethlehem Steel Company; and with Standard Oil Company of Louisiana from 1927 until 1935. Employed by The International Nickel Company, Inc., in 1935, currently he is in the development and research division.

with low-temperature applications as valve bodies, pump parts, material of fittings, headers, etc. Some values to be expected from 2.9 percent nickel steels at temperatures down to —150°F. are given in Table 4.

The field of low-temperature uses in refineries is being rapidly widened, as temperature control is now being applied to processes other than dewaxing of lubricating oils; and the question of suitable materials will become more prominent as advantages to be obtained from the uses of low temperatures are more widely appreciated. Nickel-bearing steels and alloys apparently offer a suitable material for fabrication of vessels and parts for temperatures ranging from 0 to —400°F. More data are rapidly becoming available which will permit a judicious selection of materials for different applications.

MIDDLE-TEMPERATURE RANGES

Within the temperature range from about 32°F. to about 1400°F. the bulk of alloys finds its widest application. It is within this range that corrosion is a prominent factor in the destruction and early retirement of equipment. The corrosion encountered in refineries usually sharply changes with the presence or absence of water in the liquid form. When liquid water is present, alloys of the non-ferrous type play an important part in controlling corrosion; and it is within this region of temperature, under about 300°F., that Monel is used as the lining for condenser shells and overhead lines from fractionating towers, as orifice plates in refinery gases and other utility lines, as the swing cable used in connection with storage tanks, and as a protecting surface for manholes and heads of bubble towers.

Condenser tubes offer one of the major problems in refinery metallurgy; as the organic and mineral acids accompanying the overhead material tend selectively to remove zinc from Admiralty and other copper-zinc alloy tubes—and often the water used is quite destructive to these materials. Tubes containing 70 percent copper with 30 percent nickel have made a good showing for themselves in a large eastern refinery, and their service is being extended. These tubes are very resistant to sea water and alkalies, as well as to the organic and mineral acids of the overhead material.

Ni-Resist* cast iron is becoming one of the most widely used nickel-bearing alloys employed in refineries. It finds application as a liner of reciprocating pumps and as the casing and impeller of centrifugal pumps handling naphtha, reflux, acid-treated stocks, re-gun material, acids, caustic, and a number of other materials. It is used as bubble caps and trays when intensely-corrosive conditions prevail, and has made an excellent showing in connection with the products of West Texas crudes. Valves used on the bottom of conical agitators have given excellent service when the body and gate are made of Ni-Resist and the trim is of Monel. Such valves are subject to a wide variation of concentration of acid as a result of the method of dumping of acid, and the ability of Ni-Resist to withstand attack by sulfuric acid over a fairly wide range is utilized.

Within the temperature range above, say 300°F., attack by sulfur is often the major source of destruction of metal parts. Chromium is the most effective element in resisting sulfur attack at elevated temperatures, and the alloys containing 18 percent chromium with 8 percent nickel find application within this temperature region as the trim for valves, as tubes and headers of fired coils, as the protective lining of reaction vessels and towers, as bubble caps and trays, as well as in smaller parts such as thermocouple wells, bolts, etc. The tubing of heat

* Ni-Resist is an austenitic cast iron of the composition: total carbon, 2.75-3.10 percent; silicon, 1.00-2.00 percent; nickel, 13.00-15.00 percent; copper, 5.0-7.0 percent; chromium, 1.25-4.00 percent; manganese, 1.00-1.50 percent. It is non-magnetic, and may be identified by this property.

TABLE 1

Impact Values of 2.25 to 2.50 Percent Nickel Steels and Other Nickel Steels

TYPE	PARTIAL ANALYSIS			PHYSICAL PROPERTIES				CHARPY IMPACT VALUES (Foot-Pounds)					
	Carbon (Percent)	Nickel (Percent)	Copper (Percent)	Ultimate Tensile Strength (Lb., per Sq. In.)	Yield Point (Lb., per Sq. In.)	Elongation in 2 In. (Percent)	Brinell Hardness No.	Room Temp.	—50 °F.	—75 °F.	—100 °F.	—150 °F.	—200 °F.
[1] 2.25 percent nickel steel*	0.20-0.30	2.00-2.50	....	80,000	55,000	40	....	35	21.8	..	.....	.....	.....
[2] Heat No. 11955†	0.08	1.99	....	61,500	47,000	40.5	121	63	...	62	52–63	39–40	24–30
[2] Heat No. 11956†	0.09	1.52	0.70	64,900	51,000	36.8	131	56	...	56	40–55	23–32	26–30
[2] Nickel Iron‡	0.03	3.96	....	.....	.....	....	150	..	...	..	.....	96 (—160 °F.)	41 (—220 °F.)

[1] Based on work reported by Aldridge and Shepherd, "Nickel Steel at Low Temperatures," Metals and Alloys, June and July 1936.
[2] Laboratory studies, The International Nickel Co., Inc.
Note: * Stress-relieved at 1,200 ° F. Commercial plate. Keyhole notch.
† Laboratory study. Aluminum-treated. Keyhole notch.
‡ Keyhole notch. V-notch. Normalized at 1,600 ° F.

TABLE 2

Impact Values of Yoloy at Sub-Zero Temperatures

APPROXIMATE ANALYSIS—(Percent)			CHARPY IMPACT VALUES (Foot-Pounds) KEYHOLE NOTCH				
Carbon	Nickel	Copper	104 °F.	32 °F.	—13 °F.	—58 °F.	—103 °F.
0.08	1.75	1.00	60	51	38	30	18

Data: The Youngstown Sheet and Tube Company.

TABLE 3

Impact Values of Inconel, Monel, and Nickel at Sub-Zero Temperatures

MATERIAL	STATE	CHARPY IMPACT VALUES (Foot-Pounds) 45-Deg. V-Notch		
		Room Temperature	—112 °F.	—310 °F.
Inconel (80 percent nickel, 13 percent chromium, 7 percent iron, carbon, etc.)	Hot-rolled	236	206	187
	Cold-drawn—center	33*	34*	28*
	Cold-drawn—outside	40*	38*	33*
	Annealed, 1,600 ° F.	128	126	112*
Monel (69 percent nickel, 29 percent copper)	Hot-rolled	219	213	196
	Cold-drawn—center	161	143	131*
	Cold-drawn—outside	135	129	122
	Annealed, 1,400 ° F.	215	219	207
Nickel	Hot-rolled	135	236	227
	Cold-drawn—center	185	205	210
	Cold-drawn—outside	190	236	208
	Annealed, 1,400 ° F.	216	236	234

* Specimen completely fractured. All other values are for only partly broken specimens.
Research Laboratory, The International Nickel Company, Inc.

TABLE 4

Impact Values of Cast Nickel Steel and Carbon Steel

	Chemical Composition (Percent)						Physical Properties				Charpy Impact Values (Foot-Pounds) (Keyhole Notch)				
No.	Carbon	Nickel	Manganese	Silicon	Phosphorus	Sulfur	Ultimate Tensile Strength (Lb. per Sq. In.)	Yield Point (Lb. per Sq. In.)	Elongation in 2 Inches (Percent)	Reduction of Area (Percent)	20 ° F.	0 ° F.	—50 ° F.	—75 ° F.	—150 ° F.
L-19	0.15	2.90	0.58	0.30	....	....	76,300	60,500	32.7	53.1	30	31	25	19	17
3716*	0.18	....	0.67	0.40	....	....	62,000	41,200	32.2	45.1	22	15	6	..	..
3753*	0.14	....	0.70	0.38	0.024	0.030	64,200	39,500	36.2	58.9	22.5	16.5	9	..	..

* 1 pound of aluminum used per ton.

exchangers to operate within the temperature zone above 300°F. offers a difficult problem. Some exchangers designed to allow ample expansion have made highly-successful use of the 18 percent chromium-8 percent nickel alloys, which are somewhat difficult to use in this service as a result of the comparatively high thermal coefficient of expansion. On the West Coast some tubes of Inconel (80 percent nickel; 13 percent chromium), which possess excellent resistance to sulfur by virtue of the chromium content, have been tried with what appears to to be success. The coefficient of thermal expansion of Inconel is fairly close to that of carbon steel; and, as a result, the installation of these tubes does not offer as difficult a problem as in the case of alloys with higher coefficients of expansion.

PUMPS AND COMPRESSORS

Pumps play such an important part in refinery operation and maintenance that special attention to their metallurgy is justified. As has been previously pointed out, Ni-Resist is an excellent material for pump parts if gasoline, naphthas, acid-treated stocks, and re-run materials are being handled. For a reciprocating pump handling these materials, the following is suggested:

Liner: Ni-Resist.
Piston and rings: Ni-Resist.
Rod: K Monel (full hardness).
Valves: Monel (Durabla or similar type).

For a centrifugal pump:

Casing and impeller: Ni-Resist.
Shaft: K Monel.
Wearing rings: S Monel.

Hot-oil pumps are specialized jobs, and it will usually be found that the 18 percent chromium-8 percent nickel alloys are widely used as the shafting and impellers of centrifugal-type pumps. The plunger-type pumps often utilize a high chromium (24 to 28 percent) -nickel (12 percent) alloy in the valve construction. The material for the plungers sometimes contains 18 percent chromium with 2 percent nickel and additional elements such as tungsten and molybdenum. The matter of suitable plunger material has never been satisfactorily worked out. Some attention has recently been given to sleeving plungers with heat-treated cast irons containing low percentages of nickel, chromium, and molybdenum. The rather low resistance of this material to sulfur is causing it gradually to lose place to alloys richer in chromium. The matter of handling acid sludge is constantly before the engineering groups of a large number of refineries. A suitable combination of material for a reciprocating pump to handle hot-acid sludge is given in the following:

Liner: Cast S Monel.
Rings: Monel in spring temper.
Piston: Monel (cast or wrought).
Rods: K Monel (full hardness).

FIGURE 2
Ni-Resist Exchanger Parts.
(Courtesy Kay-Brunner Products Company, Alahambra, California)

Valves: High nickel alloys such as Hastelloy D, LaBour R-55, Illium, Pioneer Metal, Durimet L, or other similar alloys.

The composition of some of the alloys mentioned above is given in Table 6.

When lubricating oils are contacted with clay, a slurry is formed that is quite abrasive; and, if acid is present, which is often the case, this slurry is rather corrosive. To handle this material suitably, a pump and its parts must be highly resistant to abrasion and fairly resistant to corrosion. Heat-treated cast irons, containing approximately 1.5 percent nickel, 0.60 percent chromium, 0.40 percent molybdenum, can be brought to a hardness that makes them quite resistant to the abrasive action. The advantage of heat-treated cast irons is that the parts can be machined prior to hardening. When higher hardness is desired, as well as superior corrosion resistance to that obtained from the composition given above, Ni-Hard* is used. Ni-Hard can be shaped only by grinding, which somewhat limits

* Ni-Hard is a cast iron containing 4 to 6 percent nickel and 1 to 2.5 percent chromium, and can develop Brinell hardness values up to 700. It is used when abrasion is a factor.

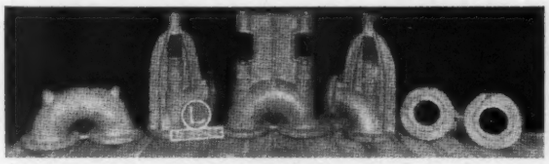


FIGURE 3
Chilling-Machine Fittings of Cast 2.50 Percent Nickel Steel for Use at Sub-Zero Temperatures.
(Courtesy Lebanon Steel Foundry Company)

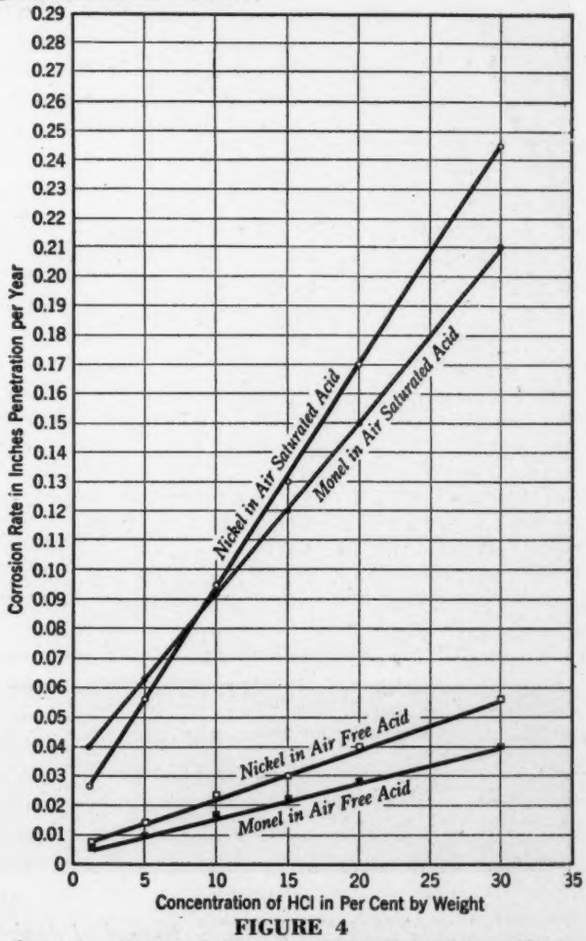


FIGURE 4
Corrosion Rates of Nickel and Monel in Hydrochloric Acid of Different Concentrations.

its usefulness. However, the art of casting this material to close tolerances is rapidly progressing, and centrifugal pumps suitable for handling slurries are available.

Compressors handling refinery gases make use of Ni-Resist as the liner for both power and compression ends, and they also employ Ni-Resist as the piston material in the compression end. Feather valves used in the compression end often contain Inconel for the flexing member. This material, by virtue of its high endurance limit and high resistance to corrosion has made a very fair showing. For other types of valve, Monel plates are used, with a high degree of satisfaction.

HIGH-TEMPERATURE RANGES

Tube supports and tube sheets, as well as flue ducts, dampers, and reaction vessels for use at temperatures above 1400°F., employ the high-chromium-high-nickel alloys. The two analyses that appear to be most widely in favor are: 25 percent chromium, 20 percent nickel; and 28 percent chromium,

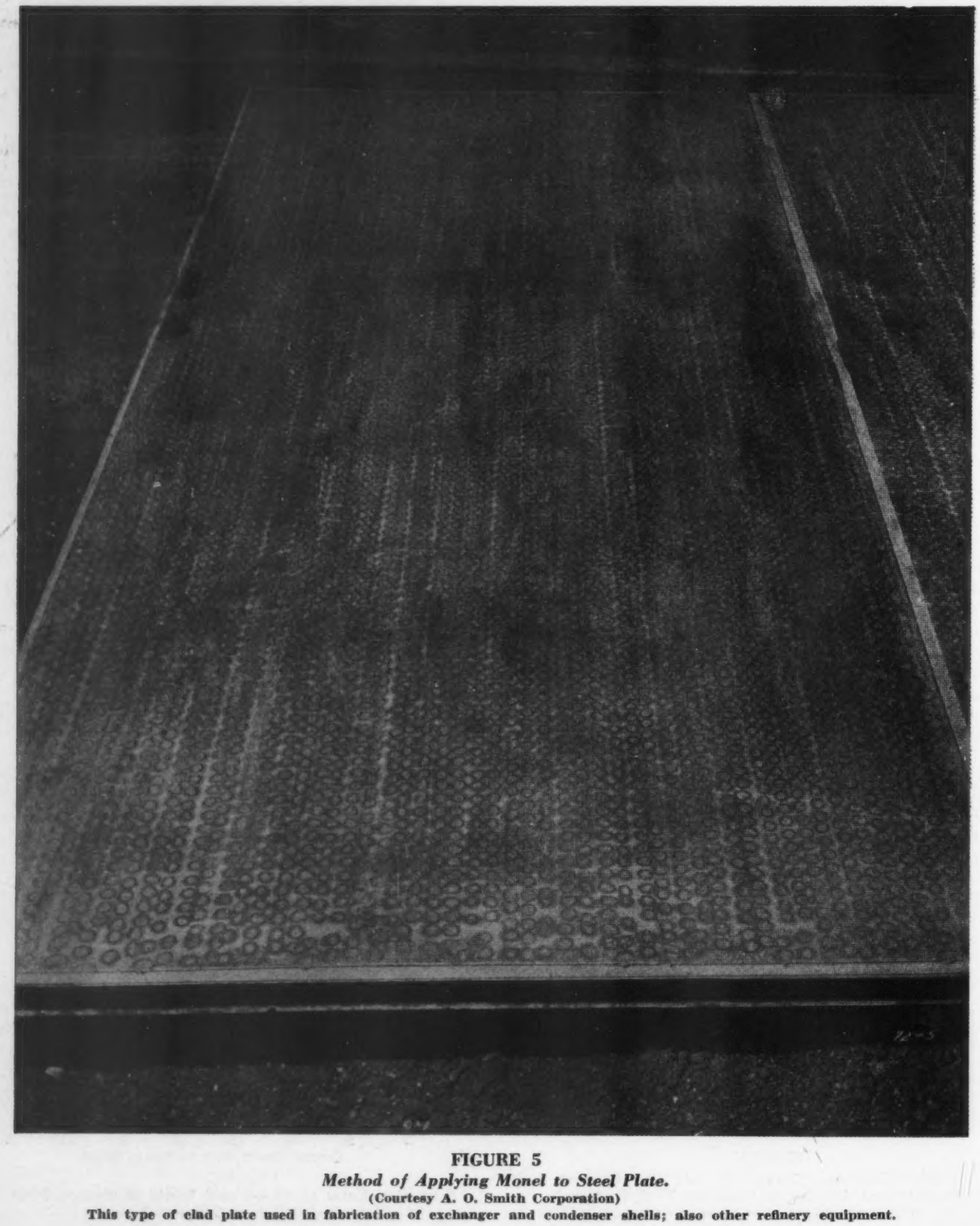


FIGURE 5

Method of Applying Monel to Steel Plate.

(Courtesy A. O. Smith Corporation)

This type of clad plate used in fabrication of exchanger and condenser shells; also other refinery equipment.

TABLE 5
Effects of Nickel on Strength of Chrome-Nickel Alloys at 1,800° F.

	COMPOSITION—(Percent)				
	Chromium	Nickel	Silicon	Carbon	Total Elongation in 2 Inches in 475 Hours
A	26.2	4.17	1.25	0.37	Flow too rapid to record. Test concluded at once.
B	25.9	10.97	1.40	0.36	0.05033 inch.
C	25.5	20.52	1.40	0.37	0.00667 inch.

Note: Specimens stressed 3,000 pound per square inch.

TABLE 6
Approximate Compositions

MATERIAL	(All Figures in Percent)							
	Nickel	Copper	Iron	Chromium	Aluminum	Silicon	Manganese	Carbon
Nickel	99.4[1]	0.1	0.15	....	....	0.05	0.2	0.1
Monel	67	30	1.4	....	....	0.1	1	0.15
"H" Monel[2]	66	29	1.5	....	....	3	0.3	0.2
"S" Monel[2]	65	29	2	....	....	4	0.3	0.2
"K" Monel[3]	66	29	0.9	....	2.75	0.25	0.4	0.15
Inconel	79.5	0.2	6.5	13	....	0.25	0.25	0.08

[1] Including cobalt. [2] Available only in cast form. [3] Capable of being hardened to Brinell hardness No. 300+ by heat treatment.

TABLE 7
Some Recently Determined Results of Effects of Sulphuric Acid on Monel at Elevated Temperatures

Time.....23 Hours
Velocity.....15.5 ft. per minute

Acid Concentration (Percent by Weight)	Temperature, 140 ° F.		Temperature, 203 ° F.		Temperature 220 ° F.
	Areated Weight Loss*	Non-areated Weight Loss*	Areated Weight Loss*	Non-areated Weight Loss*	Areated Weight Loss*
	(Milligrams Per Square Decimeter Per Day)				
5	700	...	440	...	...
10	540	...	370	...	...
20	530	35	360	65	...
35	350	...	390	...	...
40	...	20	...	65	...
50	270	...	400	...	...
60	240	25	300	100	660
70	...	120	...	460	...
75	590	...	700	...	...
80	...	200	...	500	...
85	900	...	820	...	...
96	710	740	1,400	990	...

*Note: To convert M.D.D. to inches per year multiply by 0.000164.

12 percent nickel. These, and similar compositions in which the chromium predominates, are highly resistant to oxidation and to the sulfur contained in the fuels burned. The presence of nickel enhances the oxidation-resisting qualities, and imparts a desired improvement in strength, as evidenced by short-time and creep tests. The alloys used in connection with the fired coils are usually designed to operate at 1600° F. However, they must possess sufficient reserve of the strength and resistance to oxidation to permit severe overheating during a time when a tube ruptures. The effect of nickel upon the strength of heat-resisting alloys was demonstrated in a test carried out in the laboratory of The International Nickel Company, Inc., during which specimens held at 1800° F. were stressed to 3000 pounds per square inch and the rate of flow noted during a given time. The results are recorded in Table 5.

SPECIAL REAGENTS

Certain reagents of importance to refiners have been investigated from the standpoint of their effect upon Monel, nickel, and nickel-bearing alloys; and some results are reported in the following:

SULFURIC ACID

In addition to normal acid treating, refiners make use of sulfuric acid as a solvent for separating certain constituents which can be later converted to high-octane material. An investigation, therefore, was carried out in connection with the reaction of sulfuric acid at elevated temperatures on Monel. The results are given in Table 7.

HYDROCHLORIC ACID

While hydrochloric acid as such has not entered the refineries as an important reagent, it is sometimes formed as a by-product during chlorination or as a break-down product of some reagent. The resistances of Monel and nickel to hydrochloric acid are given in Figure 4.

PHOSPHORIC ACID

Considerable investigation of phosphoric acid leads to the conclusion that the 18 percent chromium-8 percent nickel alloy, containing at least 3 percent molybdenum, is the most resistant of the commercially-available wrought alloys. The high-nickel cast alloys —which contain chromium, molybdenum, and other alloying elements, such as Illium, LaBour G-60, and similar alloys—offer a higher resistance to phosphoric acid; and, although available only in the form of castings, can be used for valve trims, valve and pump parts, and in a variety of other locations. The 18-8-3 alloy has not been successfully pierced, but there is available on the market a modified composition of 16 percent chromium, 13 percent nickel, 3 percent molybdenum which is available in tubular form.

Tubes welded from 18-8-3 have given excellent service in resisting organic acids.

NAPHTHENIC AND ORGANIC ACIDS

The 18 percent chromium-8 percent nickel-3 percent molybdenum alloy is probably the most outstanding commercial wrought material to resist these acids. Monel has shown a high order of resistance to the naphthenic acids encountered in crude oils, and can be successfully used whenever the temperature does not exceed 300° F. Above this temperature range sulfur attack may take place upon the Monel and, therefore, the 18-8-3 will be found more generally satisfactory. One important application for bolts of Monel or 18-8-3 is in connection with the hold-down strips which fasten the bubble caps to trays. Organic or naphthenic acids appear selectively to attack steel hold-down bolts, with the result that caps are released and the efficiency of the tower impaired.

CHLORINATED SOLVENTS

A number of refineries make use of chlorinated solvents, and it has been found that these solvents tend to decompose in the presence of steam and iron oxide. Monel has been found by experiment to be quite resistant to the acid liberated by the breakdown of the solvent; it also tends to inhibit the breakdown.

PHENOL, CRESYLIC ACID, FURFURAL, AND OTHER ORGANIC SOLVENTS

It has been found in some cases that attack upon carbon steel is to be expected when using the above organic solvents. The 18 percent chromium-8 percent nickel alloys are highly resistant to these solvents, and are particularly useful in the locations where the solvents are recovered from the finished products. Monel and nickel are both highly resistant to these organic solvents, and Monel is employed to protect parts of towers used in connection with the recovery of solvents.

CHLORINE

Chlorination of hydrocarbons is becoming of increasing importance in refinery circles. The equipment in which the reaction of chlorination is carried out is usually either of pure nickel or of nickel-clad steel. The nickel offers a high resistance to the reacting materials and by-products.

TESTING

Regardless of the background of experience accumulated to date, it is practically impossible to predict accurately the life and behavior of metals in refinery equipment where variations in the technique of operation are taking place. It has been found most suitable to cooperate with the metallurgical groups in refineries and, by a method of exposing standard test specimens, to work out the material most suitable for a given installation. A corrosion test spool, such as described by H. E. Searle and F. L. LaQue,[1] has been prepared by the engineering group of the Development and Research Division of The International Nickel Company, Inc., and is available to refinery engineers. These spools, containing ferrous and non-ferrous specimens of nickel-bearing and non-nickel-bearing meterials, allow a study under operating conditions; they have resulted, in a number of cases, in the satisfactory selection of materials.

BIBLIOGRAPHY

[1] H. E. Searle and F. L. LaQue, "Corrosion Testing Methods," *Prac. Am. Soc. Testing Materials*, 35 [Pt. II] 249-60 (1935). (Reprinted in *Bull. T-10*, The International Nickel Co., Inc.)

Identification and Properties of Straight-Run And Cracked Residua

[*Continued from page 282*]

effect being more pronounced than with addition of even the most aromatic solvents or cutters in like amounts. Keeping in mind the high molecular weight of the asphalt, and the colloidal nature of the systems with which we are dealing, it must be concluded that the effect is due to protective rather than solvent action.

The effect upon heater-coating indices of addition of straight residual fuels, therefore, depends upon the relationship between the solvent or protective action of the residual component and the precipitating tendency of the oil portion. In Figure 5 will be found illustrated the blending relationship of average California straight-residual and cut-back fuels, with typical cracked-tar fuels—the asphalt contents being expressed as 80-penetration residue, ASTM D-243.

The protective action of straight-run asphalt is due mainly to the so-called "oil resins" and the lighter asphaltic constituents. Gilsonite, which consists largely of resins and asphaltenes, and which unlike most mineral asphalts (asphaltites) is essentially completely soluble in cyclohexane, is a powerful protective agent. Further evidence that it is the lighter asphaltic components that contribute to stability is the existence of a definite relationship between the efficacy of asphalts as protective agents and their content of *iso*pentane-insoluble resins.

CONCLUSIONS

The percent cyclohexane-insoluble less the percent benzol-insoluble may be used as a quantitative measure of the cracked-residuum content of fuels and asphalt. In those few instances where cracked tars are undesirable, as for instance in fuels which are to be severely cut back, a reasonable specification limit offers an effective safeguard, and avoids unnecessarily severe restrictions on gravity or sediment contents. As is pointed out, much the same procedure can be used for the estimation of cracked residuum in air-blown asphalts.

In the case of residual stocks of unknown composition, analysis enables establishment of the preferred blending procedure or use.

BIBLIOGRAPHY

[1] A. H. Batchelder, "The Stability of Residual Fuels," *Proc. API*, 17 [III] 17-27 (1936).
[2] G. L. Oliensis, "Qualitative Test for Determining the Degree of Heterogeneity of Asphalts," *Proc. Am. Soc. Testing Materials*, 33 Part II, 715-21 (1933).
[3] G. L. Oliensis, "A Further Study of the Heterogeneity of Asphalt—A Quantitative Method," *Proc. Am. Soc. Testing Materials*, 36, Part II, 494-507 (1936).

Forty-First A.S.T.M. Annual Meeting

DURING the week of June 27 to July 1, inclusive, the Forty-first Annual Meeting of the American Society for Testing Materials will be held at Chalfonte-Haddon Hall, Atlantic City, N. J. To provide sufficient time for the presentation and discussion of the some 100 technical papers and reports on the program, some 18 formal sessions are being scheduled. These sessions are developed so that the papers and reports covering specific materials fields and topics will be grouped.

The outstanding feature of the meeting is to be a Symposium on Impact Testing. Other interesting groups of papers to which separate sessions will be devoted involve radiographic testing, and water for industrial uses.

Symposium on Impact Testing

The Symposium on Impact Testing is being developed jointly by the A.S.T.M. and the American Welding Society through its Welding Research Committee (jointly sponsored by the A. W. S. and the American Institute of Electrical Engineers). Two sessions of the meeting will be devoted to the several papers covering specific topics.

The symposium will be an effort to present an integrated series of papers covering the basic theories underlying impact tests, data on the factors affecting impact, and papers covering the practical application of impact tests to metals, organic plastics and welds. The symposium is prompted by the extraordinary interest in the subject. It has been developed that the impact problem consists of three related effects, (1) shape or notch effects, (2) velocity effects, (3) temperature effects. The symposium will contain papers treating each effect from the standpoint of homogeneous materials and also for welds and a discussion of the basic theory underlying all three. In addition papers will be presented on the practical application and utility of impact testing in the prevention of failures in use.

Some of the questions which it is expected the symposium will clear up or at least give partial answers to are the following: What is the purpose of an impact test? Does it measure notch sensitivity, or velocity sensitivity, or some other property of the material? To what extent have impact tests been successful in commercial practice in weeding out unsatisfactory material? While much of the work done in the last few years may not enable definite answers to these questions, it is felt the symposium will be a particularly advantageous one in presenting a review of just where various problems stand.

Broadly, the symposium will be an authoritative review of our present knowledge on impact failures and methods of test.

Water for Industrial Uses:

Another complete session of the meeting will be devoted to a series of papers on water for industrial uses. Topics to be covered in this session include embrittlement testing of boiler waters, referee and field methods for determining dissolved oxygen in water, determination of sodium in water supplies by an indirect method, removal of dissolved salts from water by exchange

The Look Box

filters, etc. A. S. T. M. Committee D-19 on Water for Industrial Uses, and the Joint Committee on Boiler Feedwater Studies are cooperating in the development of this part of the program.

Radiographic Testing:

The newly organized A. S. T. M. Committee on Radiographic Testing (designated Committee E-7) is developing a series of papers covering pertinent topics in this field. In addition to the subjects "quantitative gamma ray radiography, radiographic testing—its uses, abuses, and limitations," and "secondary radiation in the radiography of aluminum, steel and lead," certain other topics are being considered.

Other Topics:

Metals — Several interesting papers covering the properties of metals as affected by temperature and fatigue are scheduled. Some of these will cover problems of the relation of actual grain size to creep strength, temperature measurement and control in creep testing, effects of elevated temperatures on fatigue properties, and the problem of over-stressing and understressing in fatigue.

Other papers in the metals field will cover physical properties of four low alloy high-strength steels, and surface cracks on large 18 percent chromium, 8 percent nickel alloy steel castings.

In the field of cast iron there will be technical contributions pertaining to effect of size and type of specimen on the torsional properties, hardness measurement of very hard chilled cast irons and hardened tool steels, and a paper on the properties and uses of chilled iron.

The annual reports of Committee A-5 on Corrosion of Iron and Steel and Committee B-3 on Corrosion of Non-Ferrous Metals and Alloys will include valuable data which have been developed in their extensive research programs. Problems encountered in measuring the thickness and weight of coatings of hot-dip galvanized castings and forgings are to be outlined in an important paper.

Non-Metallic Materials.—In addition to a large number of committee reports, there will be numerous papers covering non-metallic materials, including contributions on the freezing-and-thawing test for building brick, and effect of shape of specimens on the apparent compressive strength of brick masonry. The effect of using a blend of portland and natural cement on the physical properties of mortar and concrete will be covered and drying shrinkage of concrete as affected by many factors will be described; also short-time creep tests of concrete in compression and hard strength between concrete and reinforcing steel. The grading-density relations of granular materials, and a study of the Wagner turbidimeter will be presented.

Other subjects to be covered in various sessions will include the effect of sulfur on the properties of asphalts.

In the field of general testing and related topics there is to be a paper outlining the uses of statistical methods as an aid in revising specifications. The examination of metals in polarized light will be discussed and means of measuring Young's modlus of elasticity by sonic vibrations will be described.

In the field of petroleum will be covered studies in the oxidation of mineral transformer oil, and an accelerated test for determining chemical stability of lubricating greases.

Conventions

JUNE 6	Oil Workers International Union, Houston, Texas.
6–9	American Society of Mechanical Engineers, National Oil and Gas Power Meeting, Dallas, Texas
12–17	Society of Automotive Engineers, Summer Meeting, The Greenbriar, White Sulphur Springs, West Virginia.
16–18	Pennsylvania Grade Crude Oil Association, Pittsburgh, Pa.
20–24	American Society of Mechanical Engineers, St. Louis, Mo.
JUNE 21-JULY 1	American Society for Testing Materials, Annual Meeting, Chalfonte-Haddon Hall, Atlantic City, N. J.
SEPT. 5–9	American Chemical Society, Milwaukee, Wisconsin.
14–16	National Petroleum Association, Hotel Traymore, Atlantic City, N. J.
OCT. 6–7	Society of Automotive Engineers, National Regional Fuels & Lubricants Meeting, Tulsa, Oklahoma.
19–21	Independent Petroleum Association, of America, Tulsa, Oklahoma.
NOV. 14–18	American Petroleum Institute, Stevens Hotel, Chicago.
DEC. 4–9	Exposition of Chemical Industries, Grand Central Palace, New York.
4–9	American Society of Mechanical Engineers, Philadelphia, Pa.

Bunn Heads Natural Gas Group

GEORGE P. BUNN, Phillips Petroleum Company, Bartlesville, has been named chairman of the 1938 Group 2 Sub-Committee on Natural Gas (wet or dry) of the Central Committee on Measuring, Sampling, and Testing Natural Gas and Natural Gasoline of the American Petroleum Institute's Division of Production. The appointment was announced by F. E. Rice, chairman of the Central Committee. Membership of the committee includes:

M. A. Abernathy, Union Producing Company, Houston; M. J. Adams, The Texas Company, Fort Worth; W. B. Berwald, U. S. Bureau of Mines, Bartlesville; G. H. Bollman, Sun Oil Com-

pany, Dallas; G. M. Davidson, Natural Gas Pipe Line Company of America, Chicago; Gilbert Estill, Oklahoma Natural Gas Corporation, Tulsa; F. D. Frank, Cities Service Gas Company, Bartlesville; W. F. Fulton, Union Producing Company, Houston;

M. L. Haider, The Carter Oil Company, Tulsa; Earl Kightlinger, Arkansas Louisiana Gas Company, Shreveport; E. C. LeFevre, Cities Service Oil Company, Bartlesville; W. H. Meir, The Atlantic Refining Company, Dallas; E. L. Rawlins, Union Producing Company, Houston; W. E. Reardon, Columbian Gasoline Corporation, Monroe, La.; G. B. Reece, Southern Counties Gas Company, Los Angeles; L. G. Rheinberger, Sinclair Prairie Oil Company, Tulsa; and F. M. Seibert, Gulf Oil Corporation, Houston;

Don Sillers, Lone Star Gas Company, Dallas; J. B. Taylor, Signal Oil & Gas Company, Los Angeles; R. D. Turner, Skelly Oil Company, Tulsa; P. G. Weidner, Stanolind Oil & Gas Company, Tulsa; D. E. West, Magnolia Petroleum Company, Dallas; B. G. Williams, Southern California Gas Company, Los Angeles; D. M. Wolfe, Standard Gasoline Company, San Francisco; and William Young, The Texas Company, Los Angeles.

Sub-committee 2-A—Analysis: Chairman, D. M. Wolfe, G. M. Davidson, E. L. Rawlins, and W. A. Simkins.

Sub-committee 2-B—Gas Measurement: Chairman, Don Sillers, G. H. Bollman, F. D. Frank, Earl Kightlinger, W. E. Reardon, D. E. West, and D. M. Wolfe.

Sub-committee 2-C—Sampling: Chairman, B. G. Williams, M. A. Abernathy, E. L. Rawlins, and G. B. Reece.

Sub-committee 2-D—Forms: Chairman, R. D. Turner, Gilbert Estill, and B. G. Williams.

Sub-committee 2-E— Gasoline content of Natural Gas: Chairman, E. C. LeFevre, W. F. Fulton, M. L. Haider, L. G. Rheinberger, F. M. Seibert, P. G. Weidner, and William Young.

Sub-committee 2-F — Open Flow Testing of Gas Wells: Chairman, W. B. Berwald, M. J. Adams, and F. D. Frank.

Forecast Motor Fuel, Crude Oil Demand, June, 1938

THE daily average supply of domestic crude oil estimated by the Bureau of Mines to meet the market demand in June, 1938, is 3,333,300 barrels. This is 15,200 higher than the estimate for May, 1938, 193,800 (5.5 percent) less than the actual daily production for June, 1937, and 5 percent less than the demand for domestic crude for that month. The reduction in the demand for crude, as compared with last year, is due to the necessary liquidation of surplus refined stocks, particularly of gasoline, as well as to further evidence of a sharp decline in the demand for residual fuel oils, which is particularly notable in the California market area.

Crude-oil production during the four weeks April 9 to May 7 averaged 3,413,000 barrels daily. During this period stocks declined 1,808,000 barrels, 456,000 barrels of which was in foreign stocks, leaving a decline of 1,352,000 barrels for domestic grades. The addition of this amount to production gives 3,461,000 barrels as the apparent daily average demand for domestic crude oil. Daily average crude runs to stills were 3,149,000 barrels during this period, or approximately the amount estimated for both domestic and foreign crude in the April forecast. Consequently the unexpected demand for almost 100,000 barrels daily must be attributed either to abnormal exports, transfers, losses, or to an increase in stocks of heavy crude in California.

Motor Fuel

Domestic demand.—The estimate for domestic motor-fuel demand for June, 1938, is 48,100,000 barrels, or 1 percent lower than the actual demand for June, 1937.

Exports. — Motor-fuel exports, based upon returns by exporters, have been estimated as 3,400,000 barrels, or 300,000 barrels higher than the estimate for May, and 315,000 barrels higher than the actual exports for June, 1937.

Stocks. — Stocks of finished and unfinished gasoline amounted to 92,320,000 barrels on March 31, 1938. According to statistics of the American Petroleum Institute, these stocks declined 1,843,000 barrels during April, bringing them to approximately 90,500,000 barrels on April 30. The heavy shipments in June in anticipation of summer gasoline demand will enable refiners to reduce their stocks materially if crude runs to stills are kept at a low figure. Accordingly, the Bureau estimates that gasoline stocks will decline 6,550,000 barrels in June, 1938, compared with an actual decline of 4,660,000 barrels in June, 1937.

Gasoline production.—Benzol and "direct" sales and losses of natural gasoline have been estimated as 950,000 barrels, making the estimated production of gasoline 44,000,000 barrels. This is distributed among the various districts as follows (thousands of barrels): East Coast, 6310; Appalachian, 1510; Indiana-Illinois, 7830; Oklahoma, 2110; Kansas-Missouri, 2360; Inland Texas, 3540; Texas Gulf Coast, 11,060; Louisiana Gulf Coast, 1380; North Louisiana-Arkansas, 940; Rocky Mountain, 1090; California, 5870.

Crude Petroleum

Runs to stills.—Natural-gasoline consumption at refineries in June is estimated as 5.8 percent of the total gasoline required, or 2,560,000 barrels. The yield of straight-run and cracked gasoline is estimated as 44.0 percent, compared wtih 43.5 percent for June, 1937. The application of this yield to the estimated straight-run and cracked gasoline production of 41,440,000 barrels gives refinery crude-oil requirements as 94,100,000 barrels, or 3,136,700 barrels daily.

Foreign crude runs. — Foreign crude runs to stills are estimated at 2,200,000 barrels, 100,000 barrels more than estimated for May.

Exports, fuel, and losses.—The estimate for crude-oil exports on the basis of returns from exporters has been decreased 100,000 barrels from the May estimate to 6,000,000 barrels.

Crude oil demand by States.—The breakdown of the total estimated daily demand for domestic crude oil of 3,333,300 barrels gives the following market demand by States of origin. As demand may be supplied either from stocks or from new production, any contemplated withdrawals from crude-oil stocks must be deducted from the Bureau's estimate of demand to determine the amount of new crude to be produced.

Penn Grade Group to Meet at Pittsburgh

THE Pennsylvania Grade Crude Oil Association will hold its fifteenth annual meeting in the city in which it was organized. A two-day program has been arranged for the association which includes crude oil producers, refiners, and marketers and jobbers of Pennsylvania oils in its membership.

On the list of speakers are a United States senator, a president of an automobile manufacturing company, marketing and advertising authorities, a trade journal publisher, in addition to several technical men who will discuss more specific phases of the industry. The association was organized in Pittsburgh in 1923; the headquarters offices are in Oil City.

W. F. Clinger, a producer and refiner of Warren, Pennsylvania, is president of the organization for the current year and will preside at the opening session. His address, a report of the past year, will be delivered at this session.

Current merchandising problems will feature the topics of most of the addresses. Men who will speak on this subject are Senator Clyde L. Herring of Iowa, who is president of a Des Moines oil company which is a member of the organization; Charles C. Parlin of the Curtis Publishing Company, Philadelphia; Warren C. Platt, publisher of the National Petroleum News, Cleveland; and John Toigo of the Chicago office of Batten, Barton, Durstine & Osborn, Inc., an advertising agency.

Harry G. Moock of the Plymouth Motor Company, Detroit, will discuss the sales outlook in the automobile field. The most recent developments in the refining industry will be the topic of an address by Dr. F. L. Carnahan of the Pennsylvania State College. The college has maintained a research program in refining for the past ten years, and the results of these investigations will form the basis for this address. Another technical subject, that of oil reserves, will be discussed by Dr. R. E. Sherrill of the University of Pittsburgh. Dr. Sherrill is in charge of a portion of the geological survey being made by the Commonwealth. C. B. McClintock, an Oil City geologist and petroleum engineer, will cooperate with Dr. Sherrill in the preparation of this paper.

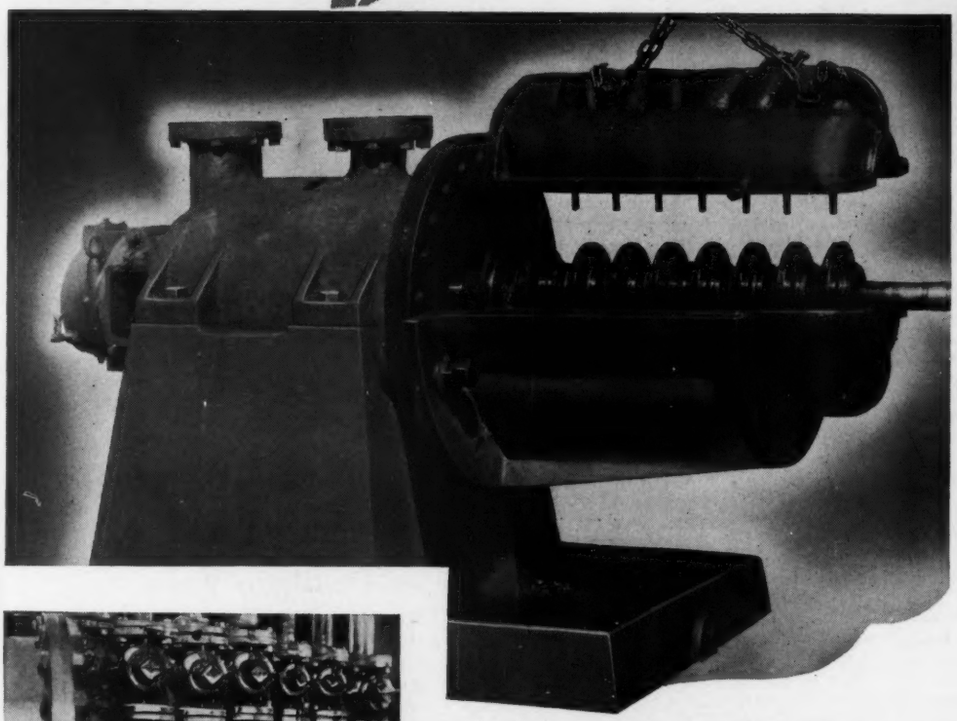
Fayette B. Dow, Washington, D. C., vice president and general counsel of the association, will discuss some aspects of the legislative situation in his address at the closing session. Directors to serve for the coming year will be chosen at the final session.

Pure Hydrocarbons Available

RECENT studies on the composition of petroleum have shown that naphthene hydrocarbons are very prevalent and very widely distributed in all petroleums. Fenske and his co-workers have shown that likely the most common of these hydrocarbons is methylcyclohexane. In view of the fact that petroleum is such an abundant source of these naphthene hydrocarbons, there is already considerable interest arising in their properties, uses and chemical reactions. To cooperate with investigators in the petroleum industry and elsewhere the Rohm & Haas Company, 222 West Washington Square, Philadelphia, has made available cyclohexane and methyl cyclohexane in very high purity, prices ranging

Safety... FROM ABRASIVE "BITES" AND CORROSIVE "BURNS"

CAST **NICKEL** IRON



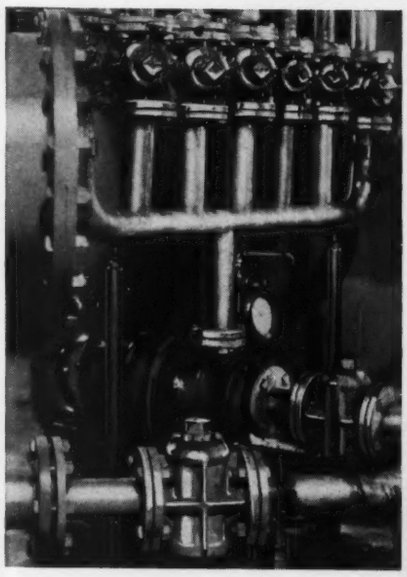
ABRASIVE CRUDE. Continuous service at pressures of 1100 p.s.i. moving 750° F. crude containing abrasive coke and sediment yet, says Byron Jackson Co., Los Angeles, maker of this turbine-driven pump at left, "First inspection of Nickel cast iron inner case, after nine months' use, shows no noticeable effects of either corrosion or erosion."

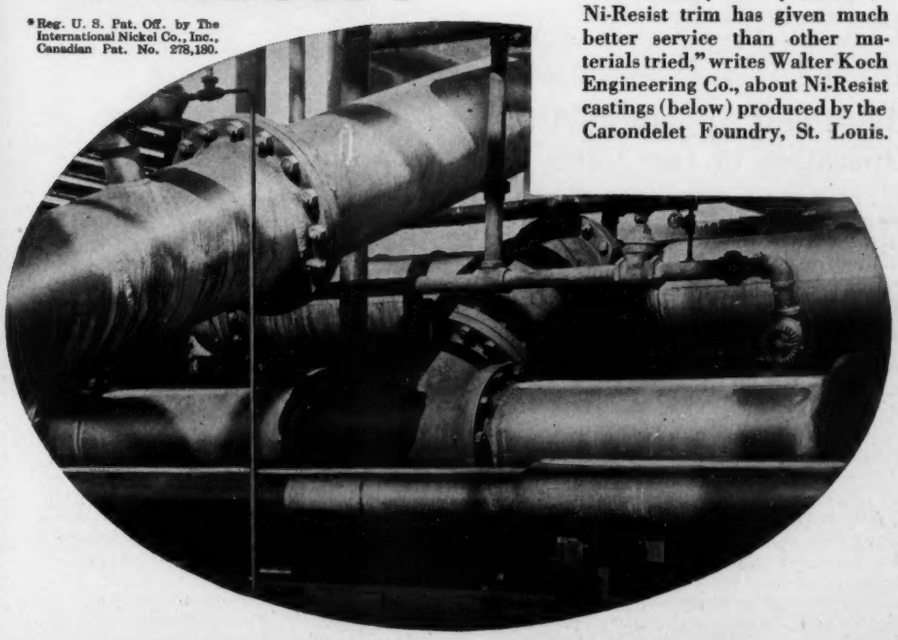
• • •

MIDCONTINENT. Oil condenser lines, raw, cracked gasoline, untreated light straight-run gasoline—you know how these uses destroy pipings and valves of plain iron. But not Ni-Resist, the patented Nickel cast iron. "For petroleum refineries . . . by far the best alloy of any kind . . . Ni-Resist trim has given much better service than other materials tried," writes Walter Koch Engineering Co., about Ni-Resist castings (below) produced by the Carondelet Foundry, St. Louis.

NI-RESIST*

*Reg. U. S. Pat. Off. by The International Nickel Co., Inc., Canadian Pat. No. 278,180.





CHEMICALS. Handling corrosives for Carbide and Chemicals Co., South Charleston, W. Va., these A.C.F. valves of fine-grained Nickel-chromium alloy iron are easily machined to close limits to retain pressure tightness, despite temperature changes. Plug valves that stay tight, resist corrosion, and require no auxiliary packing, are produced by American Car & Foundry from a dense Nickel-chromium iron.

THE INTERNATIONAL NICKEL COMPANY, INC., 67 WALL ST., NEW YORK, N. Y.

from $4.00 to $8.00 per gallon dependent on quantity. It is believed that a great many workers in the fields of chemical and petroleum technology will wish to avail themselves of this source of the hydrocarbons.

A.S.M.E. Assembles Creep Data

THE American Society of Mechanical Engineers, 29 West 39th Street, New York, is making available to engineers the first really comprehensive assembly of Creep Data on wrought and cast carbon and alloy steels including stainless steels, cast iron and some nonferrous metals, according to preliminary announcement from the society.

Creep properties may vary considerably for different steels and metals. The deformation characteristics and strength properties of metals change with temperature. For example, continuous flow (creep) occurs in service under steady loads above certain temperature ranges, which depend upon the metal. Engineers designing equipment or using metals at elevated temperatures must, therefore, have a knowledge of their creep characteristics for determining the stresses which may be safely and economically employed for different types of equipment. Books and technical periodicals have reported the results of many investigations but much data of values have remained unpublished.

Now leading laboratories of this country and Europe have released to the Joint A.S.T.M.-A.S.M.E. Research Committee on Effect of Temperature on the Properties of Metals hitherto unpublished data including more than 300 creep tests. This information has been coordinated with published data assembled by the committee for publication this month. The book, over 900 pages in length, will present 430 sheets of test data, 270 graphs and 73 tables. The society advises that this will be a limited edition and that advance orders at the prepublication price of $10.00 will determine the number of books in the edition. Price after publication is $12.00, and orders should be sent to the American Society of Mechanical Engineers, 29 West 39th Street, New York.

Dew-Point Apparatus Aids Operation of Gas Lines

EFFICIENCY of operation of natural gas transmission lines should be increased as the result of the development of a dew-point apparatus suitable for use with natural gases under pressure, by the Bureau of Mines, Department of the Interior. The temperature to which a gas may be cooled before water will begin to condense may be determined with this apparatus. This information is useful in the prevention of water condensation, which interferes with the flow of gas in the lines and, in combination with constituents of the gas, may form solid gas hydrates.

All natural gas, as it is produced from the well, carries some water in the form of vapor. The dew point, or temperature at which this water vapor will start to condense, frequently is higher than the temperature of the pipe line it enters. When this condition exists, some of the water vapor will condense to liquid as the temperature of the gas drops to the temperature of the pipe line. The apparatus just announced by the Bureau of Mines is useful in determining the dew point of the gas at the well head or along the pipe line, thus making it possible to know whether there is any likelihood that water will condense from the gas.

The gas from a compressor station usually is saturated with water vapor at a temperature considerably above the temperature of the pipe line it enters; consequently unless the gas is dried a considerable amount of water is likely to condense in the line. Many pipe-line companies are installing equipment to remove a part of the water vapor in the gas to avoid condensation in their transmission lines. The dew-point apparatus is of value in determining the efficiency and correct adjustment of such equipment.

The apparatus is suitable for working pressures up to 2500 pounds per square inch, but is equally satisfactory for use at lower pressures. It is simple in design, compact, readily portable, and easily operated. Dew points may be determined with an accuracy of 0.2° F.

The dew-point apparatus is described in Report on Investigations 3399, entitled "Bureau of Mines Apparatus for Determining the Dew Point of Gases under Pressure," by W. M. Deaton and E. M. Frost, Jr., of the Bureau's oil and gas laboratory at Amarillo, Texas. This report may be obtained without cost from the Bureau of Mines, Washington, D. C.

Elimination of Hydrates from Gas Pipe Lines

PARTIAL dehydration of natural gas, or, if that process is not available, operation of the pipe-line system at least once every few days at line pressures low enough to favor decomposition of gas hydrates are remedial measures recommended by the Bureau of Mines, United States Department of the Interior, in its latest progress report on a study of the hydrate problem in natural gas transmission lines. Hydrates, due to formation of solid material at temperatures above the freezing point of water, cause stoppages in gas transmission lines and interfere seriously with the flow of gas.

This study, which is being conducted in cooperation with the Natural Gas Department, American Gas Association, has progressed along four lines of attack, namely, review of the literature, field study of the problem, laboratory investigation of the physical and chemical properties of gas hydrates, and study of methods suitable for preventing or relieving freezeups in natural-gas pipe lines. Recently reviewed articles are cited in the report by W. M. Deaton and E. M. Frost, Jr., chemists of the Petroleum and Natural Gas Division, Bureau of Mines, presented before the meeting of the Natural Gas Department of the American Gas Association at New Orleans, La., May 9-12. Some of the articles reviewed furnish data for the International Critical Tables and others deal with rare gas hydrates such as the hydrates of argon, krypton, and xenon.

Pressure and temperature surveys of pipe lines are being made. The report points out, with reference to data obtained from actual pipeline operation, that a pressure-temperature record used in connection with a hydrate melting-point curve for the gas, will indicate the proximity or presence of conditions favorable to hydrate formation. Without the pressure record, constriction in the line caused by hydrates may be passed unnoticed.

Both laboratory and field tests show that hydrates begin to break down almost immediately following a reduction of pressure to a value below the decomposition pressure. Accordingly, if pipeline pressure does not go through a daily cycle, during which it drops below the hydrate decomposition pressure, the pipe line might be operated advantageously in a manner that would permit weekly or bi-weekly reductions of line pressure to a value below hydrate decomposition pressure — thus freeing the line for greater and more efficient throughput.

Most of the hydrate decomposition curves, as determined by experimental work in the laboratory, plot as straight lines on semi-log cross section paper. Those for natural-gas hydrates are parallel. The slope of these lines, for which an empirical equation has been determined, is constant for all natural gases investigated.

Future work under the program includes the collection of data on the composition of the hydrates as they exist under pressure and in equilibrium with the gas from which they are formed. It is desirable from a practical operating viewpoint to find some correlation of the hydrate-forming characteristics with the properties of the gas from which the hydrates are formed.

Bureau Issues Study of Distillate Wells

PRELIMINARY results of a study of the phase relations of fluids in a deep high-pressure, high-temperature reservoir of gas and light gravity hydrocarbon liquid were discussed in a report made public by the Bureau of Mines, Department of the Interior, at the convention of the Natural Gas Department, American Gas Association, New Orleans, La. A study of well performance and liquid recovery at several rates of fluid delivery, and analyses and measurement of physical properties of fluid samples taken under stabilized conditions of pressure and flow gave the data essential to the investigation.

Knowledge of the phase relations of the fluids that exist in the porous spaces of rocks constituting natural petroleum reservoirs and of the behavior of these fluids under various field conditions of operation is essential to the conservation of petroleum and natural gas and to their efficient recovery. The problem of determining whether these fluids are in the liquid or gaseous state and of recognizing the transitions that may take place as the material in the reservoir is subjected to different conditions of pressure and temperature confronts many producers today, especially in certain fields. The subject has grown rapidly in importance since the discovery of deeper reservoirs that have correspondingly higher pressures and temperatures as compared with shallower producing zones.

In the course of the tests made by the Bureau of Mines, surface samples of hydrocarbon liquid and gas were taken at the separator under conditions

Emphasizing

the importance of tube cleaning

Clean tubes don't advertise their presence by towering high above the skyline, like much refinery apparatus. But they sure do take on size and weight when the periodical operating costs are up for inspection. Clean tubes show up big on the cost sheet.

That is why a good many refinery engineers and executives think of Lagonda-Liberty Tube Cleaners in terms of the photo on the left — as big factors in operating economy. In refineries all over the country these destroyers of coke, scale and profit-eating waste are depended upon to keep tube stills, condensers, and other tubular apparatus right up on their toes. It's tough work sometimes, too—but Lagonda-Liberty Cleaners are built for tough jobs. They have a reputation of years to sustain — they've *got* to be good.

Have you a tube cleaning difficulty? Take it up with "Tube Cleaning Headquarters." Get abreast with the latest developments in equipment and methods for keeping tubes clean. Use the cooperation of specialists in tube cleaning. No obligation. Write us—ask, too, for the latest Lagonda-Liberty bulletins on refinery tube cleaning.

ELLIOTT COMPANY
LAGONDA-LIBERTY
Tube Cleaner Dept.
SPRINGFIELD, OHIO

Y-128

LAGONDA *and* LIBERTY
TUBE CLEANERS *for* REFINERIES

of stabilized flow for re-mixing in the proportions of the measured ratio of gas to hydrocarbon liquid to provide a system on which phase relations at reservoir and flow-string pressures and temperatures could be determined. A subsurface sample of hydrocarbon liquid from the well bore provided a liquid phase that in composition and properties closely approximated a liquid that could originate in the reservoir.

Although comparison of the gas-hydrocarbon liquid ratios of the well under several rates of fluid delivery did not indicate conclusively the presence of a hydrocarbon liquid phase in the reservoir, the field tests showed that hydrocarbon liquid was present in the well bore while fluid was being produced from the well.

It was concluded that part of the fluid recovered from the well was present in the reservoir in the liquid phase, and the remainder was formed during the process of production by condensation of heavy components from the original reservoir vapor phase.

The report, containing several graphs and tables that should assist engineers in developing further knowledge on this important practical problem of operation, has been published as Report of Investigations 3402, Flow Characteristics, Composition, and Some Liquid-Phase Properties of Hydrocarbon Fluids from a "Combination" Well, by C. K. Eilerts and M. A. Schellhardt. Copies are available without charge upon request from the Bureau of Mines, Washington, D. C.

Why 15 REFINERIES Recently Ordered 26 Troy-Engberg Steam Engines

Low steam consumption maintained

Moderate speed permitting direct drive or low gear ratio

Wide, flexible speed range easily controlled

DEPENDABLE

High-starting and high-running torque

No explosion hazard
Very low maintenance

Oil-free exhaust, if desired

to obtain

DEPENDABILITY ECONOMY AND CERTAIN OPERATING FEATURES

One of several Troy-Engberg Steam Engines driving pumps in the Port Arthur Refinery of The Texas Co.

Of the 26 drives referred to above, 17 were for pumps thus still further emphasizing the high rating given the modern steam engine on the question of dependability.

That the Troy-Engberg Engine is economical is amply demonstrated by the fact that many companies are getting their power at the drive shaft for ½ cent per kwh or less. And the maintenance of these engines is negligible.

As for their desirable operating features, consider those listed above. They apply equally well to horizontal and vertical engines. They are characteristics particularly useful in refineries.

The following bulletins tell the story of the modern Troy-Engberg Steam Engine. Send for copies.

SURVEY BULLETIN No. 101 telling how 43 leading companies found their average cost with the Troy-Engberg Engine to be only ½ cent per kwh. All costs were included in the survey.
Steam Engine Catalogue No. 305
Engine Control Bulletin

If you are interested in Generating Sets, send for Catalogue 107.

TROY ENGINE & MACHINE CO.
Established 1870
951 Railroad Avenue, Troy, Pa.

Liquefied Gases Sales Increase in 1937

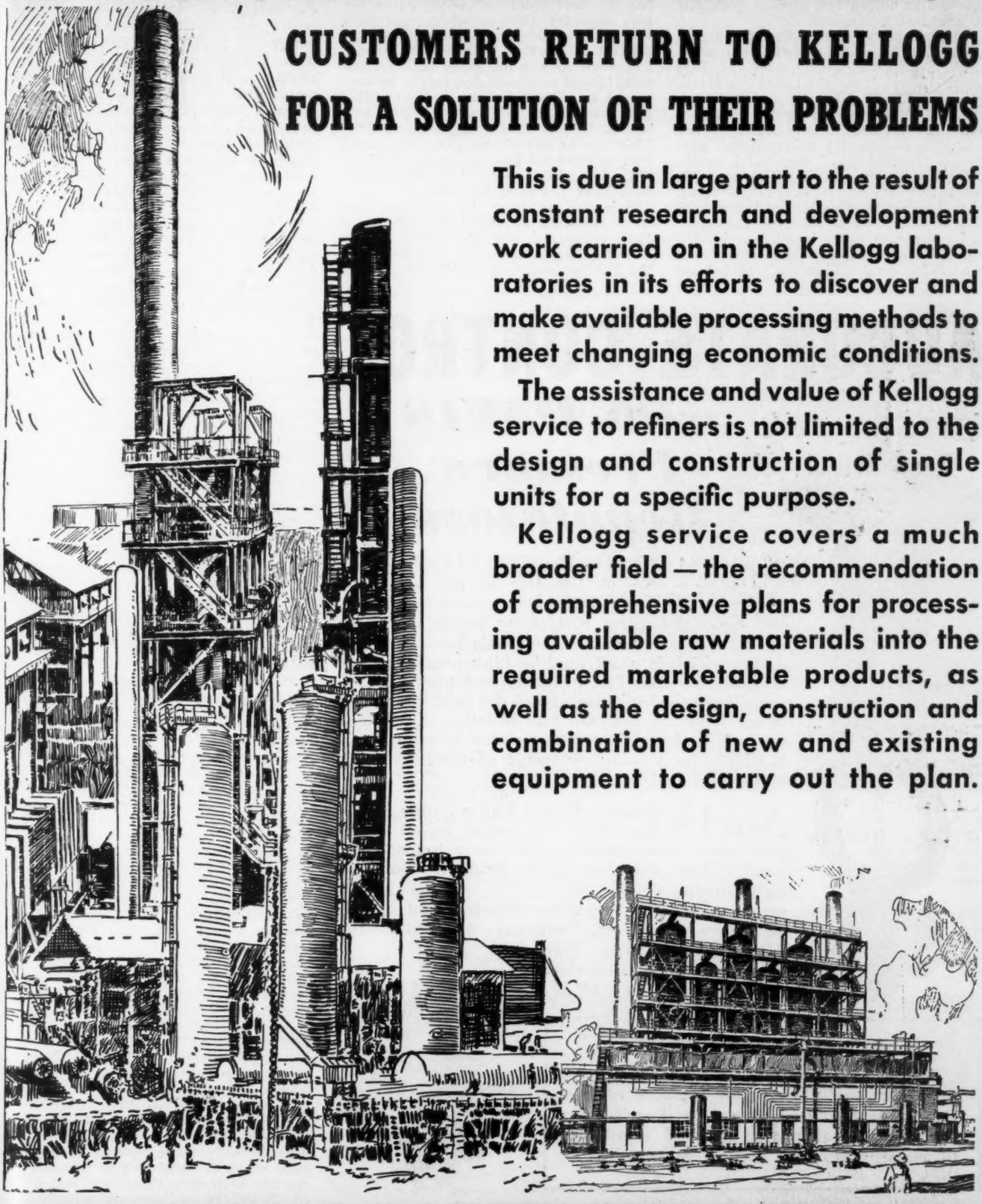
THE marketed production of liquefied petroleum gases totaled 141,505,000 gallons in 1937, according to a tabulation made from distributors' reports submitted to the Bureau of Mines. The 1937 volume of sales continued to show the sharp upward trend in the demand for liquefied petroleum gases in evidence in recent years and represents a gain of 33 percent over the 1936 total of 106,652,000 gallons. Relative gains in all major uses of liquefied petroleum gases are indicated. The 1937 totals for both domestic or "bottled gas" use and internal-combustion-engine fuel increased about 36 percent over the 1936 requirements. The quantity of liquefied gases sold in 1937 for industrial fuel and chemical manufacturing is about 28 percent above the 1936 record, while the total delivered for gas manufacturing purposes is 20 percent higher than the 1936 demand. Exports of liquefied petroleum gases to foreign countries in 1937 were reported as only 1,879,000 gallons, compared with 4,897,000 gallons in 1936. Added exports and domestic demand gives total deliveries of 143,384,000 gallons in 1937, a gain of 29 percent over the 1936 total of 111,549,000 gallons.

From about 1933 through 1936, sales of butane comprised the major portion of total deliveries: however, the 1937 totals show about equal amounts for propane and propane-butane mixtures. Propane sales in 1937 of 46,474,000 gallons represent a gain of 27 percent over the 1936 total of 36,502,000 gallons. The market demand for butane in 1937 was reported as 45,504,000 gallons, or 13 percent above the 1936 deliveries of 40,200,000 gallons. The ratio of butane sales to total deliveries of all liquefied petroleum gases declined from 38 percent in 1936 to 32 percent in 1937, while propane-butane mixtures, which constituted about one-fourth of total deliveries in 1936, increased to one-third in 1937. Quantitatively, propane-butane sales totaled 46,694,000 gallons in 1937, a gain of 71 percent over the 1936 requirements. Pentane deliveries, which are relatively unimportant in volume, increased from 2,575,000 gallons in 1936 to 2,833,000 gallons in 1937.

About half of the marketed production of liquefied petroleum gases is used for industrial fuel and in the manufacture of chemicals. Liquefied gas reported under these classifications totaled 70,102,000 gallons in 1937 compared with 54,585,000 gallons in 1936. Most of this gain must be credited to the increased use of liquefied petroleum gases in the chemical manufacturing trade, which demand virtually doubled in 1937. The use of liquefied petroleum gases as raw material in the making of chemicals is expanding at a rapid rate as their chemical structure is better understood and new processes for their conversion into desirable products are developed step by step from the experimental to the commercial stage. Liquefied petroleum gases sold to chemical plants are usually cracked or broken down chemically and then are further treated to produce ethylene glycol, alcohols, acetone and other derivatives. Still another process is based on the chlorination of pentane to produce amyl chlorides, which are then converted into other products. The sale of lique-

AS ECONOMIC CONDITIONS CHANGE

CUSTOMERS RETURN TO KELLOGG FOR A SOLUTION OF THEIR PROBLEMS



This is due in large part to the result of constant research and development work carried on in the Kellogg laboratories in its efforts to discover and make available processing methods to meet changing economic conditions.

The assistance and value of Kellogg service to refiners is not limited to the design and construction of single units for a specific purpose.

Kellogg service covers a much broader field — the recommendation of comprehensive plans for processing available raw materials into the required marketable products, as well as the design, construction and combination of new and existing equipment to carry out the plan.

THE M. W. KELLOGG COMPANY · JERSEY CITY, NEW JERSEY · 225 BROADWAY, NEW YORK

Los Angeles: 1031 South Broadway · Tulsa: Philtower Building · EUROPEAN REPRESENTATIVE: Compagnie Technique des Petroles, 134 Boulevard Haussmann, Paris, France

KELLOGG

LICENSING AND CONSTRUCTION AGENTS under United States and Foreign Patents for: Gasoline Products Company, Inc. · Cross · Holmes-Manley · de Florez · Tube and Tank · Combination · Cracking Units ••• The Polymerization Process Corporation · Gas Polymerization Units ••• The Gray Processes Corporation · Clay Treating ••• Standard Oil Company (New Jersey) · Standard Oil Company (Indiana) · Union Oil Company of California · Lube oil refining with Propane and Phenol ••• Deasphalting · Dewaxing · Solvent Extraction and Acid Treating Plants

fied petroleum gases to chemical plants, which in the past year or two has reached an important volume, bids fair to continue to expand.

The quantity of liquefied petroleum gases sold for industrial fuel increased about 8 percent in 1937 over the 1936 requirements. This relatively moderate gain in 1937 is evidently due to some extent to the slowing up of industrial activities in the second half of the year. Extensive advertising of the merits of "bottled gas," improved equipment for its storage, handling and use and better service covering larger areas, were largely responsible for the expansion in the domestic demand for liquefied petroleum gases in 1937 to 40,823,000 gallons, a gain of 36 percent over the 1936 total. Liquefied petroleum gases used by gas companies for direct distribution through their mains and for the enrichment of other gases before delivery to consumers increased from 9,371,000 gallons in 1936 to 11,280,000 galllons in 1937, or 20 percent. Liquefied petroleum gases sold for internal-combustion-engine fuel is becoming of important volume, sales for this purpose increasing from 12,476,000 gallons in 1936 to 16,987,000 gallons in 1937. This use of petroleum gases as motor fuel is confined largely to the California area, where sales of 15,000,000 gallons were reported for 1937.

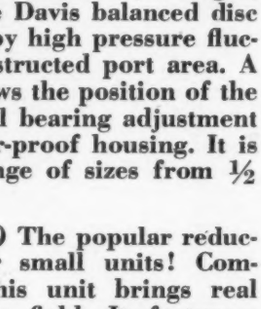
Sales of propane for all purposes were reported as 46,474,000 gallons in 1937, compared with 36,502,000 gallons in 1936. Approximately two-thirds of the 1937 quantity, or 30,436,000 gallons, were sold for domestic use, while about 14,500,000 gallons were delivered to industrial plants for fuel. Gas manufacturing companies purchased 1,077,000 gallons of propane in 1937, compared with 944,000 gallons in 1936. Minor quantities of propane were sold as raw material to chemical manufacturers, for internal-combustion-engine fuel and other miscellaneous uses. Butane, because of its higher heat content per gallon, is used principally as an industrial fuel, the quantities sold for this purpose being about 28,000,000 gallons for both 1936 and 1937. Butane gas reported for household use was 6,047,000 gallons in 1937, compared with 2,956,000 gallons in 1936. The butane delivered for domestic consumption increased over 100 percent in 1937 compared with the 1936 total, thereby repeating a similar gain made in 1936 over 1935. One development which has been important in accounting for the large relative increases in the use of butane as a domestic fuel is the active sales campaign in the south central portions of the country, where a ready supply is available from petroleum refineries and gasoline plants. Simple equipment using an outdoor tank can be installed, consequently consumers using butane can have all the advantages of natural gas at a lower cost than is possible in other sections of the country. Gas manufacturers also increased their purchases of butane substantially in 1937 receiving 7,430,000 gallons, a gain of more than 19 percent above their 1936 requirements. Butane sales for internal-combustion-engine fuel in 1937, totaled 1,715,000 gallons, or somewhat under the revised total of 2,367,000 gallons for 1936. Propane-butane mixtures are used extensively as raw material in the manufacture of chemicals and this demand accounted for over half of the 1937 deliveries. Propane-butane mixtures are also used to a large extent for internal-combustion-engine fuel, the demand increasing from 10,004,000 gallons in 1936 to 14,994,000 gallons in 1937. The domestic use of propane-butane mixtures, although relatively unimportant at the present time, increased from 2,048,000 gallons in 1936 to 3,504,000 gallons in 1937. Mixtures of these gases used in gas manufacturing were reported as 2,765,000 gallons in 1937, compared with 2,200,000 gallons in 1936. The most important use of pentane is for raw material for chemical plans; the domestic use, though increasing, was still less than a million gallons in 1937.

Cylinder and drum shipments of liquefied petroleum gases increased from 24,077,000 gallons in 1936 to 29,926,000 gallons in 1937. Shipments of this kind accounted for 21 percent of the total movement of liquefied petroleum gases in 1937, compared with about 23 percent in 1936. The larger share of the liquefied petroleum gases handled in cylinders is intended for the domestic trade, where small supplies must be furnished at frequent intervals. Domestic shipments accounted for 26,097,000 gallons (87 percent) of the total sold in small containers in 1937. Shipments of liquefied petroleum gases to large consumers, such as gas manufacturers, industrial and chemical plants are usually made in bulk in tank-cars or tank-trucks; such shipments totaled 111,579,000 gallons in 1937 compared with 82,575,000 gallons in 1936.

ACCURATE CONTROL
with DAVIS Pressure Regulators

No. 14 C **The Davis No. 14 C illustrated at the left is an advanced, modern valve for automatic pressure regulating and general control service on steam, air, gas, water or oil. It features the Davis balanced disc design which is unaffected by high pressure fluctuations and has full unobstructed port area. A valve position indicator shows the position of the inner valve. Spring and ball bearing adjustment nut are enclosed in weather-proof housing. It is available in a complete range of sizes from ½ inch to 14 inches.**

No. 13 ***(Lower Right)*** **The popular reducing valve for small units! Compact and self-contained, this unit brings real quality into the low price field. It features: tight closing single seat . . . built-in strainer . . . spring cap removable by hand . . . all parts renewable without disturbing the pipe connections. For steam, air or gas service, in sizes from ⅜″ to 2″.**



WRITE:

ASK for your copy of the Davis Pressure Regulator Service Chart. It makes it easy for you to select the type of regulator to exactly fit your service requirements.

DAVIS REGULATOR COMPANY

2515 SOUTH WASHTENAW AVE., CHICAGO, ILL.

Alcorn Company Wins Floor Tube Interference

A PRIORITY contest of five years' duration, involving radiantly heated floor tubes, was ended by the Court of Customs and Patent Appeals on April 25, 1938. Though originally involving nine different patent applications, the final contest was between George W. Watts (Standard Oil Company of Indiana) and Frank H. Praeger (Alcorn Combustion Company).

The court ruled that the disclosure by Watts of hearth tubes over an ash pit was insufficient to support patent claims covering floor tubes, below and without the currents of hot gases, absorbing heat substantially solely by radiation. Judgment was accordingly awarded to Praeger upon all issues involved in the interferences.

A typical claim, selected from the issues of the interference, is as follows:

"Oil heating apparatus comprising a chamber containing a source of heat, a second chamber in communication with and traversed by hot gases from said first chamber, tubes in said second chamber containing oil to be heated and absorbing heat substantially solely by convection, tubes in said first chamber connected to said first tubes and absorbing heat by radiation and convection, and tubes connected to said other tubes and disposed adjacent the bottom of said first chamber below the path of said hot gases for absorbing heat substantially solely by radiation."

During the early stages of the interference proceeding, the Alcorn Combustion Company introduced a patent application filed as early as January 31, 1927, with claims to tubes outside the path of gases and absorbing heat substantially solely by radiation; and received judgments of priority with respect to such claims which cover present-day types of radiant heaters. This early application has now matured into Patent No. 2,113,331, dated April 5, 1938. Typical claims are as follows:

"In an oil heating system in which heat is applied to the oil by different modes of heat transfer in different zones while flowing in succession through banks of oil-conducting heat-absorbing tubes within said zones, the method of heating the oil to elevated discharge temperature which comprises, producing in unobstructed radiant view of the tubes of a bank within one of said zones a current of hot combustion gases having substantial initial velocity therein, utilizing the directional effects upon said gases of their initial velocity and of their tendency to rise within said one zone to direct said current of gases in positive avoidance of, and along a path adjacent and substantially parallel to, said bank of tubes within said one zone, transferring heat of said gases substantially solely by radiation to said tubes within said one zone and reducing the temperature of said gases, and transferring heat, at least in part by convection, from said gases of reduced temperature to one of said banks of tubes within another of said zones.

In a system of heating oil, the combination of a heating chamber, means for directing streams of hot combustion gases toward and into convective heat exchange with opposite walls of said chamber, said walls absorbing heat from said gases and reradiating the absorbed heat, and a bank of heat-absorbing tubes disposed intermediate said walls, without the paths of said streams of hot gases, any given cross-section of said bank of tubes receiving heat substantially solely by direct radiation from both of said oppositely disposed walls."

J. S. Alcorn, president of Alcorn Combustion Company, assignee of the Praeger application, states that the company is willing to grant non-exclusive licenses to all who are now using, or who in the future may wish to use, structures or methods covered by patents owned by Alcorn Combustion Company.

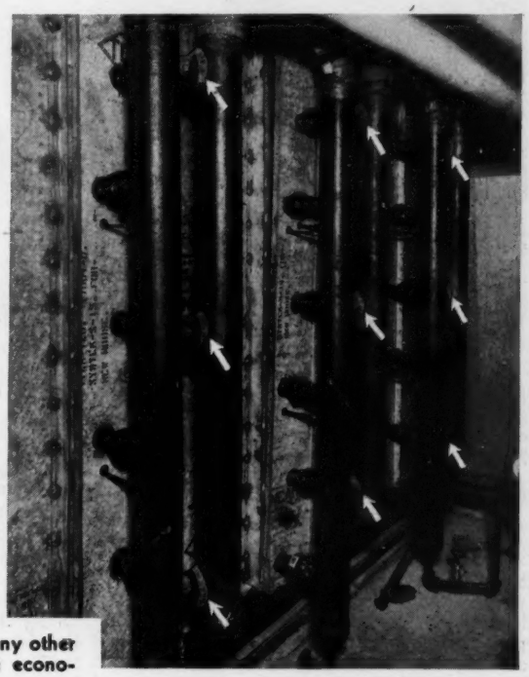
Tank Volume Tables

THE United States Bureau of Standards announces publication of a pamphlet giving the volume of liquid in filled or partly filled horizontal cylindrical tanks. The pamphlet was printed to meet requests, particularly from the petroleum industry, for such information. Copies may be secured from the office of the Superintendent of Documents, Government Printing Office, Washington, D. C. Price 5 cents.

The names "WeldOlets" and "ThredOlets" are Bonney trade marks registered in the United States Patent Office. Full patent coverage for designs, principles and construction has been granted in the United States and foreign countries.

For Air Conditioning

BONNEY WELDOLETS THREDOLETS



WHEN welded piping was specified for the air conditioning system at the New House of Representatives Office Building, Washington, D. C.—the largest air conditioning contract ever awarded—Bonney WeldOlets and ThredOlets were specified for making branch pipe connections.

Engineers and contractors recognize the fact that they are correctly designed, make stronger outlets than any other method of making take-offs and are economical to buy and install.

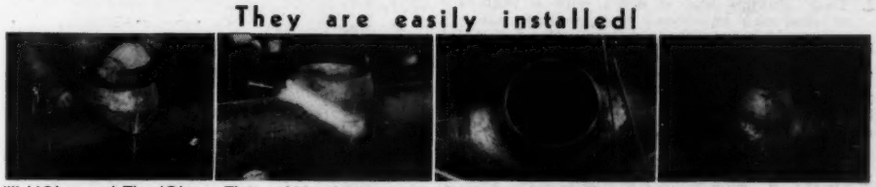
WeldOlets and ThredOlets eliminate all cutting, threading and fitting of the main pipe. They make branch pipe connections of full pipe strength that are absolutely leak-proof. Their funnel-shaped outlets improve free flow conditions and reduce turbulence and friction to a minimum.

Your piping job may not be air-conditioning, but regardless of what it is for—whether new construction or maintenance—WeldOlets and ThredOlets will make better take-offs at less cost than any other fittings.

Standard fittings are drop-forged of steel, but they're available in Toncan Iron, Wrought Iron, Brass, Monel, Everdur, etc. to meet every piping need.

Improve your next piping job and save with these fittings. Once used, you'll standardize on them. For full information write for Bulletin WT23 or see your nearest distributor.

They are easily installed!



WeldOlets and ThredOlets are quickly and easily installed. Select the position of the outlet anywhere on the main pipe, mark center lines and tack the fitting into position.

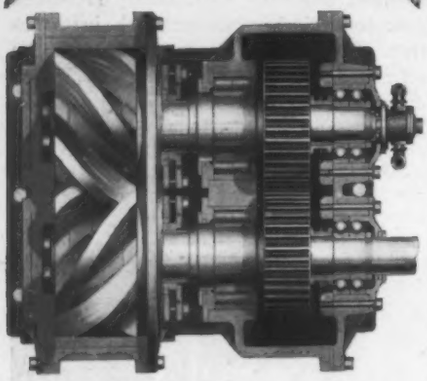
Then weld by electric-arc or oxy-acetylene method. A leak-proof joint of full pipe strength is obtained.

On two-inch outlets or larger the button is removed after installation. A full inspection of the inside of the joint is possible when WeldOlets and ThredOlets are used.

A simple Vee weld is used for attaching the branch when WeldOlets are used. If ThredOlets are used, the branch is screwed into position.

BONNEY FORGE & TOOL WORKS, Allentown, Pa.
WELDOLETS · THREDOLETS
. . . *Welded Outlets for Piping* . . .
Stocked by Leading Distributors

KINNEY



KINNEY HELIQUAD MAIN CARGO PUMPS

—for barge and tanker service

Popular wherever oil is refined, it is only natural that Kinney Heliquads should prove popular also for pumping all grades of petroleum product cargo from gasoline to fuel oil.

All Bearings and Timing Gears Outside Pump Chamber

These pumps have bronze cylinder and head liners and are unusual in the rotary pump field in that all bearings and timing gears are entirely outside of the pump chamber; and yet have only two stuffing boxes instead of the usual four.

Bearings are designed to maintain the rotors central in the pump housing, regardless of the position of the boat. This prevents metallic endwise contact.

Regular Kinney Heliquad Features Maintained

1. Labyrinth ring to the suction side of the pump, thus requiring that pumps be packed against suction pressure only.
2. Each stuffing box is fitted with a lantern or seal ring connected to a suitable lubricator which provides a simple method of applying lubricant to the stuffing boxes.
3. The packing runs on stellite shaft sleeves.

WRITE FOR INFORMATION.
ADDRESS NEAREST OFFICE

KINNEY MANUFACTURING CO.
3539 WASHINGTON ST., BOSTON, MASS.
NEW YORK: 30 Church Street
CHICAGO: 1202 Buckingham Bldg.
DALLAS: 808 Santa Fe Bldg.
PHILADELPHIA: 725 Commercial Trust Bldg.
LOS ANGELES:
1333 Santa Fe Avenue

PUMPS

▼ PLANT ACTIVITIES ▼

Cracking: Rodessa Oil & Refining Company, Shreveport, Louisiana, has started construction of a new cracking unit. The plant is designed under patents of the Forward process and is to produce high-octane-rating motor fuel.

Enlarge: East Texas Refining Company at its Rodessa, Miller County, Arkansas gasoline plant is enlarging plant capacity through installation of eight more compressors, additional absorbers and a new cooling tower. Reported cost is $150,000. Present capacity of the plant is 50,000 gallons a day.

Gasoline Plant: Portex Oil Corporation is nearing completion of its 15,000-gallon compression-type natural gasoline plant in the Logansport gas field of Shelby County, Texas. Residue gas is to be injected into the producing sand.

Enlarge: Mohawk Petroleum Corporation, Fruitvale, California, has completed remodeling and enlarging one unit at the refinery for increased capacity to produce road oils and asphalts. Plant capacity was increased to 8000 barrels a day. Two 1000-horsepower boilers were added to the steam-generation plant. Two new cracking units were completed recently and the company is now installing a 5000-barrel ethyl blending plant at reported cost of $30,000. E. L. Rogers is refinery superintendent. The company recently signed license agreement with Universal Oil Products Company, to operate its existing cracking facilities under Dubbs cracking patents.

Tankage: Sinclair Refining Company, East Chicago, Indiana, has let contract to Western Gas Division of The Koppers Company, for additional tankage which includes a riveted and weld-caulked, water-sealed gas holder with capacity of 750,000 cubic feet, and 25 by 18 feet sweating tank, three 26 by 10 by 8 feet open-top run-down tanks, and two 12 by 8 feet 6 inches hot-water tanks. Tanks are all to be of welded steel. The gas holder is to be completed in October and the tanks in August of this year.

Refinery: Petrol Corporation, Long Beach, California, is reported planning erection of a new refinery this year to cost around $500,000.

Refinery: Edco Refining Company, Santa Maria, California, is building a new 1000-barrel refinery to be completed this summer.

Power Plants: Shell Oil Company and Pacific Gas & Electric Company, at Martinez, California, and Union Oil Company of California and Pacific Gas & Electric Company at Oleum, California, have arranged for construction of separate 44,000-kilowatt steam generating plants at the points mentioned. Likewise, Tide Water Associated Oil Company and the Pacific Gas & Electric Company have made similar arrangements for a like plant. Each of the installations are being erected at reported costs of $5,000,000, to be completed this coming fall.

Expansion: The Atlantic Refining Company, Philadelphia, has announced an expansion and developments program requiring capital expenditures of $28,000,000 to be undertaken this year. The program will cover acquirement of additional properties in oil producing areas, marketing activities and improvement of operations at the company's refineries at Atreco, Texas, and Philadelphia, and additions to the tanker fleet.

Lease: Anglo-Canadian Oil Company, Calgary, Alberta, Canada, has leased the refining plant of Central Refiners, Ltd., and a 750-barrel skimming unit has been erected. The company is reported planning erection of a cracking unit.

Refinery: Lake Arthur Oil Refinery, Inc., has completed a 1000-barrel skimming plant on the south side of Lake Arthur, Calcasieu Parish, Louisiana, to process South Roanoke and Woodlawn high-gravity crudes.

Operating: Dale Refining Company, Dale, Texas, has started operating its new 1000-barrel skimming plant, operating on crudes from northern Caldwell County to produce gasoline, naphthas, kerosene, tractor fuels, furnace oils and other fuels. R. E. Goode is refinery manager.

Gasoline Plant: Hamman Exploration Company, Bay City, Matagorda County, Texas, has let contract to Western Construction Corporation for construction of a gasoline absorption plant with capacity reported at 15,000 gallons a day and at cost of approximately $100,000.

Repressuring Plant: American Liberty Oil Company, Dallas, Texas, is planning construction of a natural gasoline extraction and oil sand repressuring plant which will remove distillate and strip gas and return gas to the producing horizon in the Gradeland field, Houston County, Texas.

Refinery: British American Oil Company, which has interest in production in the Turner Valley, Alberta, Canada, field is reported looking at plant sites in Calgary, East Calgary and High River with view to establishment of a new 5000-barrel refinery.

Operating: Yale Oil Corporation, Kilispell, Montana, has completed construction and started operating its new 1000-barrel refinery. Clayton Burke is superintendent.

Expansion: Trinidad Leaseholds, Ltd., Trinidad, is completing a refinery expansion and modernization program which includes erection of new cracking facilities and a polymerization installation.

Enlarge: United British Oilfields, Trinidad, whose operations are managed by Anglo-Saxon Petroleum Company, Ltd., is reported planning expenditure of $1,750,000 for expansion of refining facilities and exploration of new producing properties.

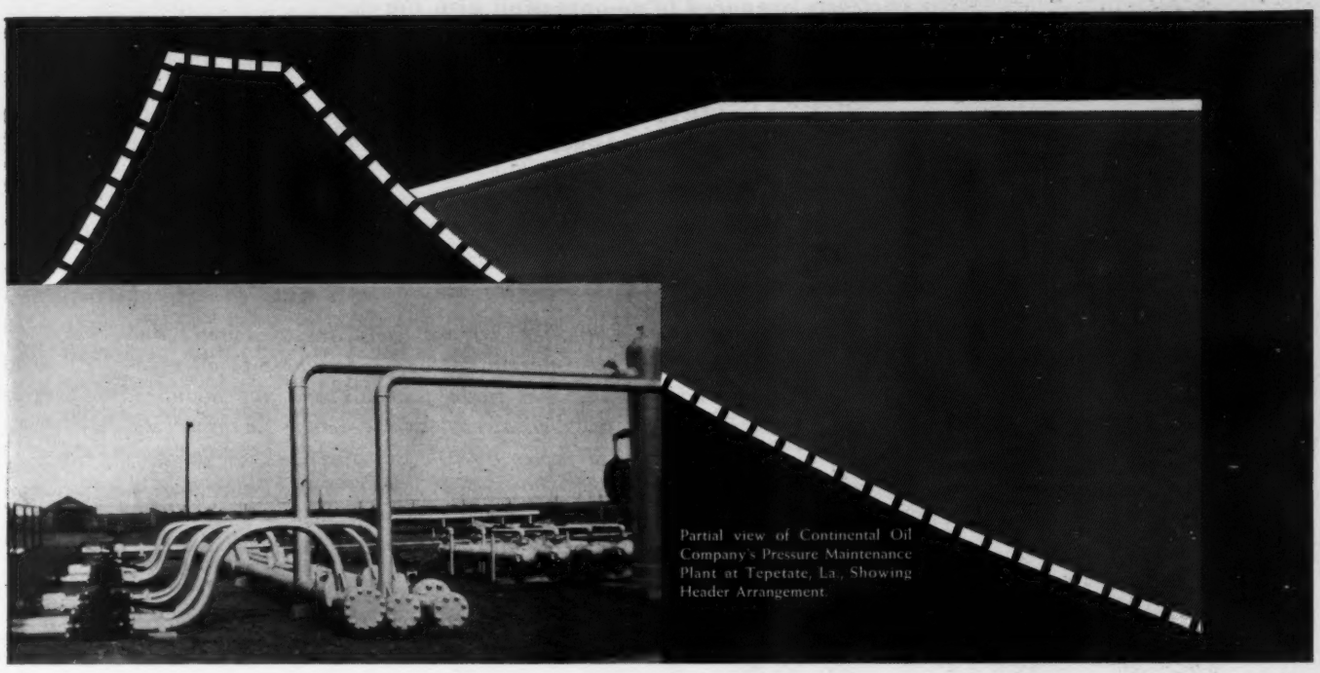
Gasoline Plant: Union Oil Company of California and Superior Oil Company are building a 60,000,000 cubic foot absorption type natural gasoline plant at Rio Bravo, California, at estimated cost of $500,000.

Compression Plant: Richfield Oil Corporation is building a new compressor plant at Wilmington, California.

Gasoline Plant: Wilmington Gasoline Company is building a 20,000,000 cubic foot absorption type natural gasoline plant at Wilmington, California, to be completed this summer.

Gasoline Plant: St. Helens Petroleum Company is planning erection of a new 25,000,000 cubic foot gasoline plant of the absorption type in the Montebello field, California.

LEVEL YOUR PRESSURE CURVE



Partial view of Continental Oil Company's Pressure Maintenance Plant at Tepetate, La., Showing Header Arrangement

WITH PRESSURE MAINTENANCE!

Increase the life and value of your investment; secure the maximum recovery of oil, gas and natural gasoline; prolong the life of your wells; return dry gas underground for conservation and future use! Secure these and many other added profit-building advantages by leveling your pressure curve through repressuring!

Through this value-proven method, dry gas is returned to the oil bearing sand under pressure sufficiently high to guarantee complete penetration. Pressure maintenance, through repressuring, permits a constantly close approach to the original rock pressure. Records exist of supposedly depleted fields being returned to high productivity with the recovery of many added millions of barrels of oil through the use of this method. Natural gasoline production is maintained at maximum for the greatest number of years and added profits result from elimination of blow-off and the consequent upbuilding of an underground gas reserve which assures continuance of profitable gasoline plant operation.

We are prepared to construct such plants for any pressure condition based upon the requirements of your production engineers. We invite inquiry.

PARKHILL-WADE
973 NORTH MAIN STREET
LOS ANGELES CALIFORNIA

AFFILIATED WITH
THE STEARNS-ROGER MANUFACTURING CO.
1720 CALIFORNIA STREET • DENVER, COLO.

SCIENCE AND TECHNOLOGY

Abstracts prepared in co-operation with the

REFINER AND NATURAL GASOLINE MANUFACTURER

by

THE LESLIE LABORATORIES

Traver Road, Ann Arbor, Mich.

under the supervision of

DR. E. H. LESLIE and DR. H. B. COATS

The abstracts here presented are selected from the current literature of science and technology to afford reference to fundamental information not easily available to all readers. Abstracts of articles appearing in readily obtainable trade journals are not included. Photostat copies of original articles will be supplied at cost by the Leslie Laboratories. Complete or limited bibliographies covering special topics by title, by abstracts, or in complete manuscript, will also be prepared and furnished at reasonable cost by the Laboratories.

Fundamental Physical and Chemical Data

Liquid-Vapor Phase Equilibrium Relations in the Ethane-n-Heptane System. W. B. KAY, *Ind. & Eng. Chem.* **30** (1938), pp. 459-65.

A knowledge of the equilibrium composition of liquid and vapor in complex hydrocarbon mixtures is of importance in the design of fractionating and absorption equipment in the petroleum industry. The P-V-T-X relations at the liquid- and vapor-phase boundaries in the ethane-n-heptane system were evolved from measurements on a series of solutions varying in composition from pure ethane to pure n-heptane. Temperature compositions, or T-X diagrams of the coexisting liquid and vapor at constant pressure were constructed, and a comparison was made with those computed by means of the solution laws. The results of this comparison show that Raoult's and Dalton's laws, corrected for departure from ideality of the gas and liquid phases by the use of fugacity, apply reasonably well to these solutions until pressures in the neighborhood of the critical pressure of n-heptane are approached. In the critical region the solution laws fail completely. Equilibrium constants were obtained for ethane and n-heptane. Those for ethane at high temperatures differ considerably from those predicted; those for n-heptane are in good agreement with those predicted except at high pressures.

Thermodynamic Properties of Substances as a Function of Reduced Temperature. I. Latent Heat. Vapor Volume and Vapor Pressure of Water. H. A. FALES AND C. S. SHAPIRO, *Jour. Am. Chem. Soc.* **60** (1938), pp. 784-94.

The authors studied the question of expressing latent heat as a function of reduced temperature alone, and also studied the theory of corresponding states of van der Waals. The study of the volume-ratio as a function of reduced temperature leads to the formulation of a relationship between latent heat and reduced temperature alone that holds with n fundamental limits. This study also led to a functional relationship between pressure and volume and reduced temperature alone that likewise holds within required accuracy. Previous work on these general subjects is reviewed and discussed in some detail.

Thermodynamic Properties of Substances as a Function of Reduced Temperature. II. Vapor Pressure of Liquids and the Principle of Corresponding States. H. A. FALES AND C. S. SHAPIRO, *Jour. Am. Chem. Soc.* **60** (1938), pp. 794-805.

The authors apply the equation of reduced pressure to a large number of substances with a view to determining some modification of the principle of corresponding states that might embrace different types of compounds. The reduced vapor pressures of chemically different substances were found to be expressible in terms of reduced temperature within the limits of experimental error. The form of the vapor pressure function was entirely analogous to that of the volume ratio. The fact that the reduced vapor pressures are given accurately by the proposed equation leads to the possibility of defining the behavior of all substances when compared at equal reduced temperatures. At equal reduced temperatures the reduced vapor pressures of two substances are related definitely to each other. The relating coefficients are, in general, different from unity and are exponential functions of temperature and of the parameters of the equation. The coefficients become unity only at the critical point, this being the only temperature at which the properties of substances are identical. At other temperatures the coefficients increase with decrease of reduced temperatures.

Vapor Pressures of Solvents. D. H. KILLEFFER, *Ind. & Eng. Chem.* **30** (1938), pp. 477-9.

Nomographic charts are given for the vapor pressure of solvents. One chart covers those solvents boiling below 90° C.; and one, those boiling from 90° C to 150° C. To determine the vapor pressure at any temperature, it is necessary only to connect the temperature on the left-hand scale and the point characteristic of the compound with the vapor pressure scale by means of a straight line. The manner of preparing the nomograph is explained.

Mutual Solubilities of Hydrocarbons. II. The Freezing Point Curves of Dotriacontane (Dicetyl) in Dodecane, Decane, Octane, Hexane, Cyclohexane and Benzene. W. F. SEYER, *Jour. Am. Chem. Soc.* **60** (1938), pp. 827-30.

The freezing point curves of four paraffin hydrocarbons dotriacontane (dicetyl) were studied. The paraffin hydrocarbons used were hexane, octane, decane and dodecane. Curves were also determined for dicetyl-benzene and dicetyl-cyclohexane. After a concentration of about 0.4 N is reached the solute appears to exert its influence in determining the shape of the freezing point curve. It is thought that this may be the result of the separation of mixed crystals from the solution. The experimental data support the validity of Raoult's law.

Critical Solution Temperatures of Mixtures of Gasoline, Propyl Alcohol and Water. E. W. ALDRICH, *J. Research Natl. Bur. Standards* **20** (1938), pp. 9-16. (Research Paper No. 1060.)

It was found that the water tolerances of mixtures of gasoline and propyl alcohol are greater than those of mixtures of gasoline with ethyl alcohol. In mixtures containing propyl alcohol the second phase will be solid if separation occurs below —15° C.

Water Tolerances of Mixtures of Gasoline with Ethyl Alcohol. O. C. BRIDGMAN AND E. W. ALDRICH, *J. Research Natl. Bur. Standards* **20** (1938), pp. 1-8. (Research Paper No. 1059.)

The author has developed equations for calculating the water tolerance of any mixture of gasoline with ethyl alcohol from critical solution temperature measurements on a few mixtures with a particular gasoline. Critical solution temperatures of mixtures of known composition can be calculated.

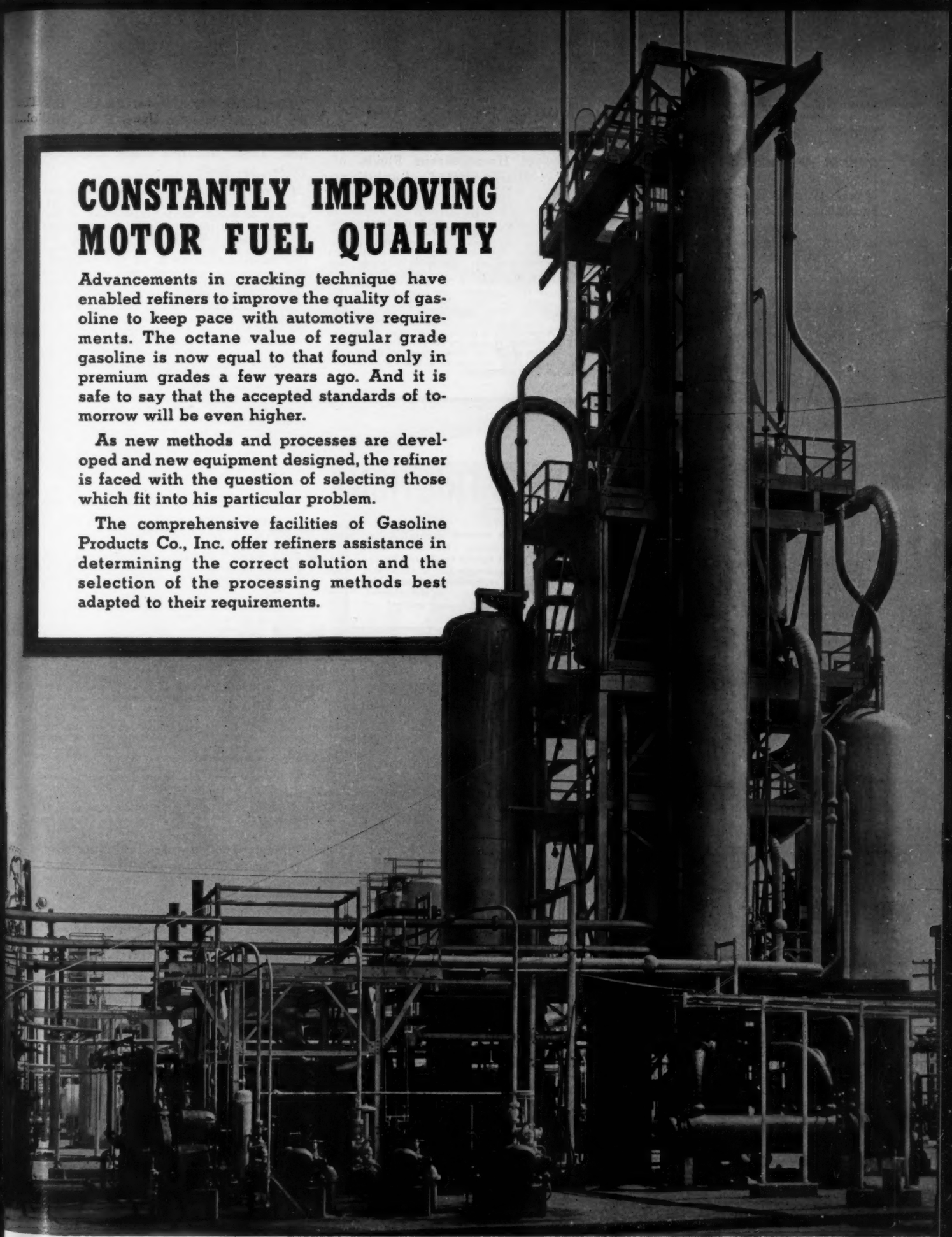
Chemical Compositions and Reactions

Nitrogen Compounds in Petroleum Distillates. XI. Isolation of 2, 3-Dimethyl-8-ethylquinoline from the Kerosene Distillate of California Petroleum. C. L. KEY AND J. R. BAILEY, *Jour. Am. Chem. Soc.* **60** (1938), pp. 763-5.

The crude organic bases used in the investigation and called "kero" bases, were from a residual sulfur dioxide extract obtained in refining California kerosene by the Edeleanu process. The isolation of 2, 3-dimethyl-8-ethylquinoline from the complex mixture of bases is described. The structure assigned to this product was confirmed by synthesis. 2, 3-Dimethylquinoline and 3-methyl-8-ethylquinoline were obtained from the first mentioned base by indirect dealkylation at positions 8 and 2, respectively. The first of these derived bases is one of five keroquinolines that were previously isolated in the Texas Laboratory. The structure of the second derived base, a new quinoline homolog, was established by synthesis.

The Thermal Decomposition of Alicyclic Compounds. I. The Decomposition of Cyclohexene and Some Simpler Hydrocarbons. F. O. RICE, P. M. RUOFF AND E. L. RODOWSKAS, *Jour. Am. Chem. Soc.* **60** (1938), pp. 955-61.

Cyclohexene can be decomposed practically quantitatively into 1, 3-butadiene and ethylene by heating at about 10 mm. pressure and 800° C. The rate of decomposition of ethylene and 1, 3-butadiene is negligible under these conditions as compared with cyclohexene. A test for free radicals shows that the rate of removal of metallic mirrors by the fragments from cyclohexene is of a lower order as compared with the rate of removal by open chain compounds such as acetone. The author assumes that the primary step is a rupture of a C-C bond in the beta-position to the double bond, followed by



CONSTANTLY IMPROVING MOTOR FUEL QUALITY

Advancements in cracking technique have enabled refiners to improve the quality of gasoline to keep pace with automotive requirements. The octane value of regular grade gasoline is now equal to that found only in premium grades a few years ago. And it is safe to say that the accepted standards of tomorrow will be even higher.

As new methods and processes are developed and new equipment designed, the refiner is faced with the question of selecting those which fit into his particular problem.

The comprehensive facilities of Gasoline Products Co., Inc. offer refiners assistance in determining the correct solution and the selection of the processing methods best adapted to their requirements.

LICENSES granted under United States and Foreign Patents for: Cross, de Florez, Holmes-Manley, Tube and Tank Cracking Processes, Uni-Coil Injection Process and Combination Cracking Units
Licensing Agents: THE M. W. KELLOGG CO., Jersey City, New Jersey, or its *European Representative:* COMPAGNIE TECHNIQUE des PETROLES, 134 Boulevard Haussmann, Paris, France

Gasoline Products Company
INCORPORATED

decomposition into ethylene and butadiene. No radical chain mechanism occurs as in open chain compounds.

Direct Oxidation of Oils by Air; Formation of Peroxides. P. MONDAIN-MONVAL AND S. MARTEAU, *Ann. Combustibles Liquides* **12** (1937), pp. 923-8.

Oils were contacted with air by being flowed slowly through a slightly inclined heated glass tube. Oxidation was evidenced by the typical white fumes and luminescence. The products contained alkyl peroxides in quantity. The oxidation reaction started at 150-225° C., and is marked at 180-300° C. The lowest temperatures of oxidation were shown by 6 mineral oils, paraffin, and cod-liver oil, followed in order by linseed, neat's foot, olive, rape-seed, earth-nut, and castor oils. The authors believe that explosions in air compressors are attributable to the formation of these peroxides.

Manufacture: Processes and Plant

Flow of Homogeneous Fluids. M. MUSKAT, *McGraw-Hill, London,* 1937, pp. xix + 755.

Although of primary interest in connection with the problems of petroleum production, the subject-matter of a comprehensive work on the flow of homogeneous fluids through porous media is also of some interest in connection with refinery problems. The book is divided into four main parts. The first is the foundation upon which the remainder of the work is built. The second treats problems of fluid flow in the steady state. The third part treats typical cases of non-steady flow. Solutions of typical problems of gas flow are considered in the fourth part. The work as a whole constitutes a valuable addition to the knowledge of the flow of fluids. It is in no sense an elementary textbook, but rather treats the subject in a mathematical and thorough-going manner.

Metal Knit Cloth Tower Packing and Its Use in Plate Columns. F. C. VILBRANDT, EDWIN SHUFFLE, JR., AND S. B. ROW, *Trans. Am. Inst. Chem. Engrs.* **34** (1938), pp. 51-69.

Use of metal cloth as a tower packing and in conjunction with bubble-cap and plate columns is described. Knitted metal cloth of No. 30 gage has friction factors varying between 223×10^{-7} and 1041×10^{-7} at flows of air between 13.2 and 37.7 ft. per min., and at water flows between 0 and 8.4 lb. per min. per sq. ft. of packing. The tests were made in an 18-in-diam. stoneware tower with calming sections. Murphree plate efficiencies decrease with increased vapor velocity in the case of a bubble-cap column, the knit cloth-packed column, and the combination of the two. The use of knit metal packing above the bubble cap plate increases the efficiency. However, the limiting superficial column velocity is 0.5 ft. per sec. A column packed with knit cloth packing alone gives efficiencies slightly higher than those obtained with the bubble-cap column and slightly lower than those of the combination column. The limiting superficial column velocity for the column equipped with knit cloth packing alone was 0.82 ft. per sec. Pressure drop through the column was greater with bubble caps than with copper knit cloth packing at the lower velocities.

Heat Exchangers for Chemical Process Applications. K. B. MILLETT, *Ind. & Eng. Chem.* **30** (1938), pp. 367-72.

The author notes that the commercial availability of corrosion-resistant material enables the maker of chemical and corrosive products to reduce manufacturing costs by saving heat through the use of efficient and durable interchangers. The data required by the manufacturer in order to make the most appropriate selection of apparatus, together with the salient factors to be considered in preparing specifications of duty to be performed, are outlined. Design features, such as efficient and practical structures for cross flow and leak-proof longitudinal baffles, are discussed and illustrated. The resistance method of determining the surface required is described. Special designs for high-pressure operations, such as the rotatable breech-block type, are described. Designs using "extended" or "compensated" surfaces are discussed. A tubular construction, without shell enclosure but with a series of metallic transferring yokes between the two for use with dirty or corrosive fluid, is described and illustrated. A table is given that shows heat units transferred per dollar of purchase price for a range of exchangers between 5000 and 5500 square feet of surface is included for various duties and materials.

Mean Temperature Difference Correction in Multipass Exchangers. F. K. FISCHER, *Ind. & Eng. Chem.* **30** (1938), pp. 377-83.

The literature on the subject of the mean temperature difference in multipass exchangers is first reviewed. Underwood's equations for one shell pass and two tube passes, and for two shell passes and four tube passes are repeated. An equation is derived for an exchanger having one shell pass and one parallel- and two counterflow-tube passes. As this equation requires a trial and error solution, the results are tabulated. The results are extended to exchangers having two, three, and four shell passes, and are given in tables and also in the form of curves. A comparison shows that an exchanger having one parallel- and two counterflow-tube passes per shell pass has a considerably better mean temperature difference than one having an even number of tube passes per shell pass. The relation that the correction factor across each shell pass is equal, and is equal to the over-all correction factor is derived. A few general rules to observe in determining the true mean temperature difference are: (1) When the number of tube passes per shell is even, the M.T.D. is independent of the direction of flow of the shell fluid in each pass. (2) When the number of tube passes per shell is odd, the M.T.D. depends on the direction of flow of the shell fluid in each shell pass and is greater when the counterflow tube passes exceeds the parallel flow tube passes in each shell pass. (3) In multishell pass exchangers the over-all M.T.D. depends on whether the flow of fluids between the shell passes is counter or parallel flow. (4) The equations available for solving the true M.T.D. applying to multipass heat exchangers can be made general by letting the T

A TIGHTER SEAL WITH LESS FRICTION?
SEA RINGS are completely automatic. The flexible lip is held tightly to the rod by the pressure on the work stroke, but releases on the return. Unnecessary friction is eliminated, there is less wear on both rod and packing.
YES!
when you use
SEA RINGS

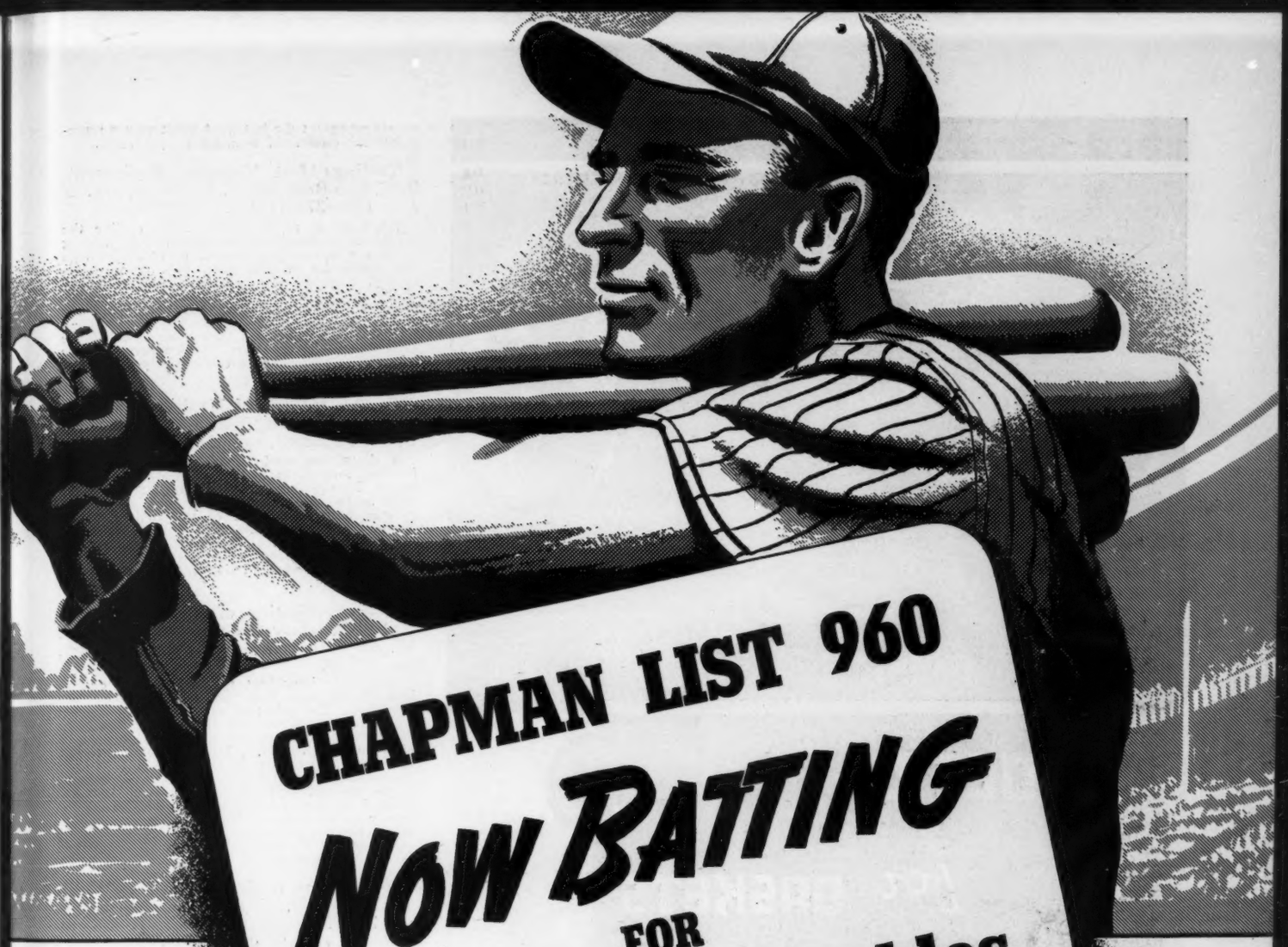
INCREASED operating efficiency and less time lost for repacking . . . that is the record J-M Sea Rings have made in plants throughout the country. Three features explain their exceptional service—proper composition, correct design and rugged construction. And these same three features are characteristic of all packings in the complete J-M line.

Johns-Manville, largest manufacturer of asbestos products, is well equipped to make packings of unusual quality. J-M Packings are the result of 60 years' research and experience in the development of materials specifically suited to various mechanical equipment and service conditions. No matter what your packing problem is, there is a J-M Packing that can handle it efficiently, dependably and economically.

The J-M Packings Catalog will help you select the right packing for every requirement in your plant. For your copy, write Johns-Manville, 22 E. 40th St., N. Y. C.

JM JOHNS-MANVILLE PACKINGS & GASKETS

AVAILABLE ON PHONE CALL AT YOUR NEAREST DISTRIBUTOR



CHAPMAN LIST 960
NOW BATTING
FOR
Small Valve Troubles

Take the weak spots out of your small valve lineup and put in a valve that can hit. Backed by a five year contract, you can put this valve any place on your field and be sure that it won't muff a play. It handles the hot ones—pressures up to 800 lbs. at 750°F.—or the cold working pressures to 1500 lbs. And it's always in the pink of condition—parts are stainless steel. There's never a substitution—no need for stock replacements. Nor time out—repacking is done under full pressure, with the valve in the open position.

BRANCH OFFICES

New York
Philadelphia
Pittsburgh
St. Louis
Salt Lake City
San Francisco
Syracuse
Tulsa
Atlanta
Boston
Chicago
Denver
Cleveland
Detroit
Houston
Los Angeles

The **CHAPMAN VALVE**
MANUFACTURING COMPANY
INDIAN ORCHARD MASSACHUSETTS

You can sign up the CHAPMAN LIST 960 in 8 sizes—¼" to 2"—at factory and warehouses. In special steels also. Throw your requests to the nearest Chapman office.

GOETZE

for GASKETS

NEW BULLETIN
FOR USERS OF RINGS

Goetze Gaskets for Ring Joint Flanges are available in Armco Ingot Iron, 4-6 Chrome Alloy Steel or any of the several other desirable metals or alloys.

Brinell hardness of 80-90 for Armco Ingot Iron and below 130 for 4-6 Chrome Alloy Steel is carefully maintained by heat-treating. This assures proper flow of gasket material without damage to flange surfaces and without undue stress on bolting.

Each gasket is individually and accurately machined within close tolerances to secure perfect fit. Every step, from metal analysis to final inspection is rigidly controlled to guarantee strict adherence to every detail of specifications.

New Bulletin 51 makes it easy to order . . . Send for your copy.

GOETZE GASKET & PACKING CO., INC.
8 Allen Avenue New Brunswick, N. J.

values represent the hot fluid and t values represent the cold fluid terminal temperatures.

Testing Heat Transfer Equipment. R. C. GUNNESS AND J. G. BAKER, *Ind. & Eng. Chem.* **30** (1938), pp. 373-6.

The purpose of the article is to outline the experimental procedure required for the testing of heat exchange equipment, particularly from the standpoint of the economics of heat recovery. Methods of measuring the rates of flow of the fluids, the temperature, and the pressure drop, are described. The optimum cycle for cleaning exchangers is discussed. This is applied in a particular case to a cooler, where a balance exists between the cost of cleaning and the cost of cooling water. A bibliography of several references is given.

Double-End-Fired Naphtha and Gasoline Re-Forming Furnace. *Ind. & Eng. Chem.* **30** (1938), pp. 398-9.

A double-end-fired naphtha and gasoline reforming furnace is briefly described, and illustrated in six cuts. Special alloy steels were used in the tubes and headers and alloy steel casings for the support of the radiant tubes. Walls and bridge walls were air-cooled. Many oil and gas burners were placed along each firing front to ensure even distribution of heat and accurate control of temperature in all parts of the furnace.

The Application of Automatic Control to Refinery Process Operations. S. W. ADEY, *Jour. Inst. Pet. Tech.* **24** (1938), pp. 125-39.

The more important type of process control instruments and their underlying theory are described. The selection of methods of control and the installation of instruments are discussed. The importance of close cooperation between plant operator, designer and instrument manufacturer is emphasized. Stabilizing and Automatic Re-Set Devices, and their significance in the control of continuous processes, are explained. It is noted that some instruments serve purely as labor-saving devices, while others definitely improve operating efficiency and quality of product. This economic aspect of the subject is briefly reviewed.

Production of Solid Paraffin (Wax). R. LIEBETANZ, *Seifens.-Ztg.*, **64** (1937), pp. 794-95.

Needle crystals that process more easily than platelet crystals in sweating operations are obtained by crystallizing the wax from a solution containing a small quantity of phenol. A highly viscous non-crystallizing distillate was treated with sulfuric acid, and then with a 0.1% solution of phenol in benzine.

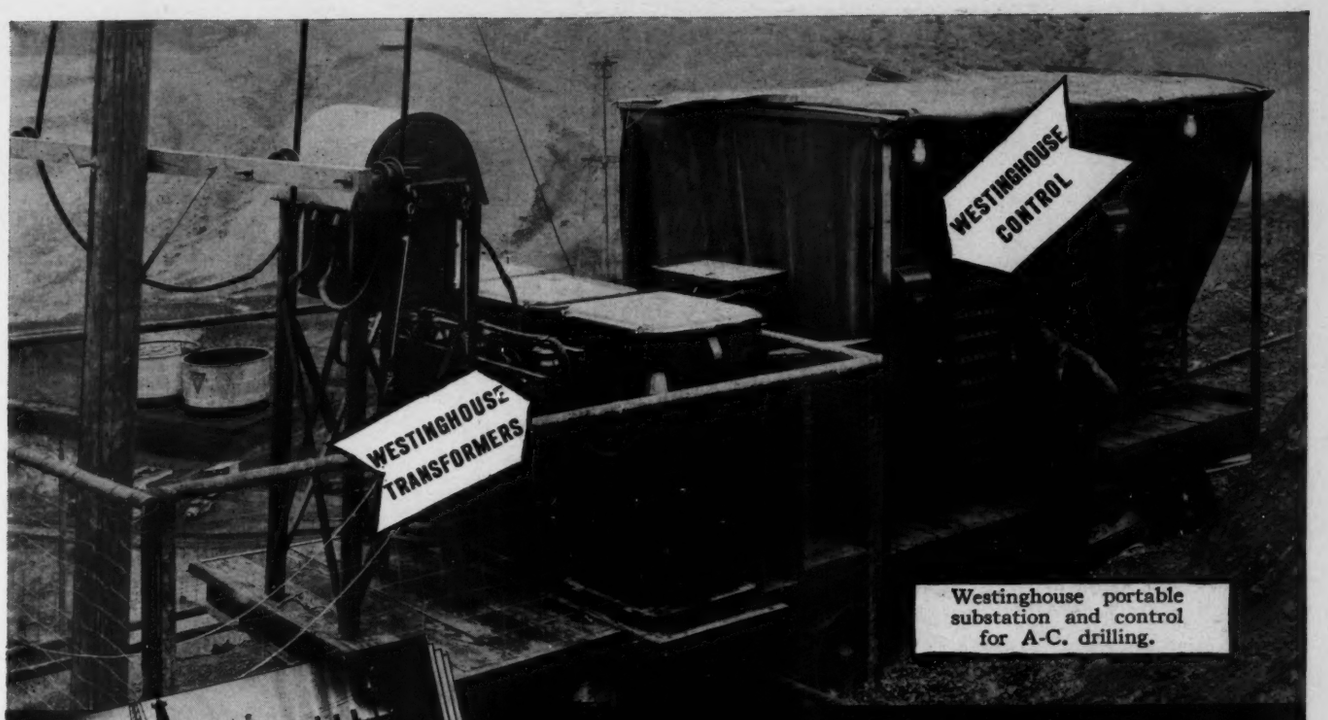
Toxicity of Industrial Organic Solvents. Compiled by ETHEL BROWNING under direction of Committee on The Toxicity of Industrial Solvents—Report No. 80 of Industrial Health Research Board of Medical Research Council. *H. M. Stationery Office*, pp. iii + 382.

The large scale and increasing use of organic solvents lends considerable importance to the general subject of the toxicity of organic solvents. Dr. Browning has summarized existing works on the subject. Most of the common organic solvents are covered, and useful descriptions are given of their industrial applications and toxic effects, if any, on animals and on man when this is known. The numerous references given considerably increase the value of the work.

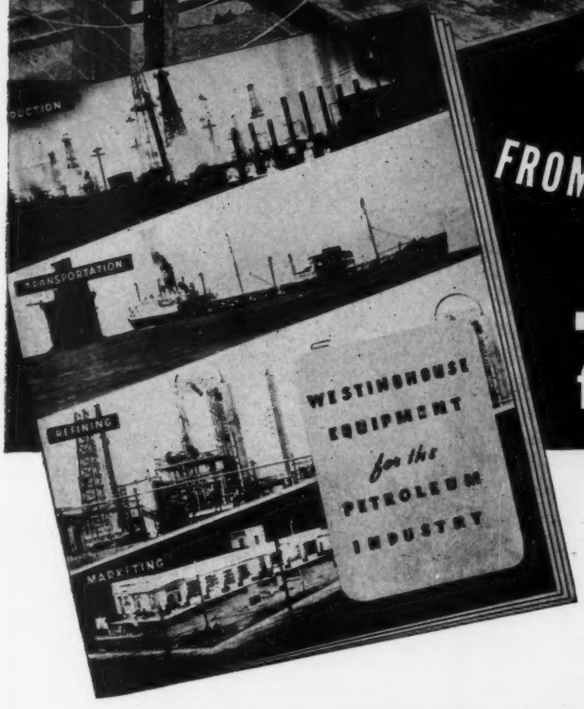
Products: Properties and Utilization

Propane, Butane and Related Fuels. *U. S. Bureau of Standards*, Letter Circular No. 503 (Supercedes LC. 292), Sept. 1, 1937.

The composition, manufacture, properties and methods of distribution of commercial propane and butane are described. Methods of delivery and storage are discussed in connection with its domestic and industrial use, as well as types of burners. The leading distributors of liquefied gases, with trade names and compositions of products, are listed. Attention is called to the disadvantage of the use of butane and propane in cold climates owing to insufficient vaporization. Variation in the composition of vapours from mixed fuel gases restricts their use for domestic purposes, although they are suitable for the enriching of city gas. For a small town gas supply the greater volatility of propane as compared to butane outweighs the greater cost,



Westinghouse portable substation and control for A-C. drilling.



FROM DRILLING RIG TO SERVICE STATION

.. ONE SOURCE

for everything electrical

From production to marketing, Westinghouse specialized products and counsel assure the petroleum industry of correct equipment for the job, properly applied for safe and efficient operation.

How Westinghouse is aiding other producers, refiners and marketers — how electrification is being applied in new drilling, refining and pumping projects — what the newest developments are in methods and equipment — are surveyed briefly and pictorially in a way that will interest you, in the booklet at the left. Ask your local Westinghouse representative for your copy, or write for booklet 2160. Westinghouse Electric & Manufacturing Co., Dept. 7-N, E. Pittsburgh, Pa.

GET YOUR COPY OF THIS NEW BOOK

Illustrated applications of Westinghouse equipment for the petroleum industry from drilling rig to service station. Ask for booklet 2160.

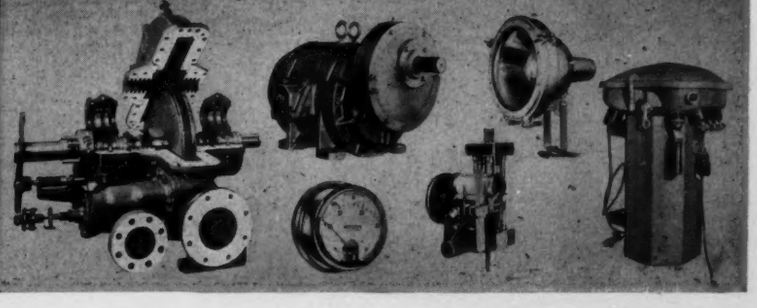
J-93827

W WESTINGHOUSE ELECTRIC

Westinghouse

Electrical Partner of the Petroleum Industry

A FEW TYPICAL PRODUCTS FROM THE COMPLETE LINE OF WESTINGHOUSE EQUIPMENT FOR THE PETROLEUM INDUSTRY



MAXIM SILENCERS

Meet Your Requirements

Model SC2

The wide variety of Maxim models permits the selection of a silencer to **exactly** fit the specifications. For internal combustion engines of all description, for compressors, vacuum pumps and blowers, there is a Maxim Silencer to do the job efficiently.

To eliminate the danger from flying sparks, and at the same time eliminate exhaust noise, the SC2 and the SC are available. For natural gas engines, subject to exhaust line explosions, use the BRX HEAVY DUTY TYPE. And if you have a small portable rig, we can offer the BRM2 or the MM. Our Engineering Department is at your disposal; submit your problem today.

The

MAXIM SILENCER COMPANY

Dallas, Texas Hartford, Conn.

but for larger systems butane is to be preferred. In order to prevent condensation, butane is supplied mixed with air, the resulting mixture having a heating value frequently as low as 520 B.Th.U.s per cu. ft. Underground storage presents problems, corrosion being the most serious. The recommendation is made that no gas lighter than pentane be stored underground.

Nitrogen Oxides in Internal-Combustion Engine Gases. T. K. HANSON AND A. C. EGERTON, *Proc. Roy. Soc.* (London) **A163** (1937), pp. 90-100.

The quantity of NO_2 and total oxides of nitrogen were determined for a Diesel engine for different crank angles and at different loads and jacket temperatures, and in a Delco engine under knocking and non-knocking conditions. Corresponding cylinder gas temperatures were also taken. In the Diesel engine, oxides appear at the beginning of combustion, rise to a maximum of 0.06%, which percent corresponds approximately to the gas temperature, and then decline because of absorption by water and by oil. As load and jacket temperature increase, the amount of oxides increases. In the Delco engine, it was found that the amount of oxides increased during the expansion stroke to values greater than corresponding to the gas temperature. This indicated the existence of long-lived and excited molecules. The NO in the residual gas explains the increase in NO_2 in the compression stroke. When knocking occurs, the concentration of oxides increases greatly, reaching a figure of 0.5%. The quantity of oxides dissolved in the lubricating oil is sufficient to catalyze the oxidation and gumming of the oil. The analytical methods used in the work are described.

The Practice of Lubrication. T. C. THOMSEN, McGraw-Hill, London, 1937, pp. xiv + 638.

The book is a third edition of the author's well-known work on practical lubrication. Six chapters are devoted to the theory of lubrication, methods of testing and descriptions of lubricants. Among the subjects treated in the remaining thirty chapters are: a discussion of bearings in general; bearing lubrication; lubrication problems peculiar to different types of machinery, including steam turbines, stationary horizontal and vertical engines, and marine and locomotive types. A few of the chapter headings include: textile machinery, compressors, refrigerating machines, gas engines, diesel engines, steel and tinplate mills, and the "gasoline engine."

An Experimental Investigation of the Use of Oil for the Treatment of Coal. R. A. SHERMAN AND J. M. PILCHER, *Trans. Am. Soc. Mech. Engrs.* **60** (1938), pp. 97-109.

A report is made on an investigation of the treatment of coals with oil for the reduction of dust and after varying periods of exposure to weather. Five oils that are commonly sold for the treatment of coal, and one petroleum, were used in treating two coals, one from the Island Creek seam in Logan County, West Virginia, a representative coal of firm structure from the Appalachian field, and the other a No. 6 seam Illinois coal. In practice, the oil is usually sprayed on the coal as the latter falls from the loading boom to the car. This procedure was simulated in the laboratory. The oil was applied at 200°F. in amounts ranging from 0.85 to 30 quarts per ton. The coals were exposed to the weather in small bins on the roof. The technique in determining dustiness is described. It is shown that the results check those approximately calculated from Stokes' law for the terminal velocity of particles. It was concluded that oil having a stable viscosity of 200 seconds at 100 was much more effective initially in reducing dustiness than oil having a viscosity of 100 seconds at 100 in the treatment of Island Creek coal. Oil having a viscosity of 600 seconds at 100°F. was more effective than 200 second oil in treating Illinois No. 6 coal. Petrolatum having a melting point of 131°F. was slightly more effective than the 600 second oil. The dustiness of treated coal increases after storage. The rate of increase decreases with increase in the quantity of oil applied. The Illinois coal was found less amenable to effective dustless treatment than the Island Creek coal. The amount of oil required for effective dustless treatment of coal varies with the size of the coal, as would be expected. The removal of the finer sizes, such as —20 mesh, naturally reduces the quantity of oil required.

Structure in Asphalts, Indicated by Solvent-Treated Surfaces. R. N. TRAXLER AND C. E. COOMBS, *Ind. & Eng. Chem.* **30** (1938), pp. 440-3.

Asphalts are usually considered to be protected lyophobe sols made up of soft, rather fluid material as the medium, and harder carbon compounds of higher molecular weight as the dispersed lyophobe portion. The soft medium

72-Octane

That is the average of regular grade gasoline sold in this country today, Oil and Gas Journal finds It sets a new high record

Do you think you can sell ordinary gasoline against such competition—and get the price for it?

You have to have high octane and you have to get all you can in the refinery—lead can't do it all

Dubbscracking is the way to make high-octane gasoline—and get the yield, too

"The so-called octane race has turned into a march," says Oil and Gas Journal

Right—and Dubbscracking is leading the march

Universal Oil Products Co
Chicago, Illinois

Dubbs Cracking Process
Owner and Licensor

VIGILANT
Liquid-Level
REGULATOR

LIQUID LEVEL
and
Flow In or Out
under positive
Remote Control

In the operation of Stills, Vaporizers, Bubble Towers, and Dephlegmators, a continuous inlet or outlet flow and a constant level of condensates can be definitely secured by installing a differential-type Vigilant Liquid Level Regulator on the side of the tank, and the control valve on the inlet or outlet line as required. Control works on compressed air, steam, water or gas. Catalog on request.

THE CHAPLIN-FULTON MANUFACTURING CO.
28-40 Penn Avenue Pittsburgh, Pa.

W-S
FORGED STEEL
FITTINGS

For complete satisfaction on lines carrying oil or gas under high pressures and high temperatures, specify W-S Forged Steel Fittings.

They are bored from solid steel forgings, have sharp accurately cut threads and every fitting is carefully inspected and tested.

You will find them definitely stronger, longer lived and more dependable under the most severe conditions.

The better service insured by W-S Fittings is expressed in dollars saved in maintenance.

Write for Bulletin A-3.

THE WATSON-STILLMAN CO.
ROSELLE, N. J.

or continuous phase is usually known as petrolenes or malthenes, the dispersed materials as asphaltenes. The protective colloids, which are regarded as unsaturated hydrocarbons with a high sulfur or oxygen content, are frequently known as asphaltic resins. A study of flow characteristics indicates that asphalts possess varying degrees of internal structure, depending upon the source of material, method of processing, and temperature at which the rheological test is made. Asphalts that show distinct anomalous flow characteristics, as manifested by a high rate of age hardening and marked elastic properties, give surface design when treated with partial solvents, such as ethyl ether, or 86° Be. naphtha. The essentially viscous asphalts do not show design. The presence of the surface pattern may be regarded as an indication of the presence of structure in an asphalt. A number of illustrative photographs are reproduced.

Ignition Quality of Diesel Fuels. *Jour. Inst. Pet. Tech.*, **24** (1938), pp. 176-79.

The ignition quality of a diesel fuel is a measure of the relative time required for combustion to start after the commencement of injection; the shorter the time the higher the ignition quality. High ignition quality indicates ease of starting and smoothness of running, but the ignition quality of a fuel is not necessarily an indication of its combustion quality in all types of compression ignition engines. Furthermore, hot-bulb engines have special requirements, as have engines that use spark ignition for heavy oils. No form of test is suitable for rating fuels for these engines except direct tests on the engines themselves. Two methods of test have been described by the Institution of Petroleum Technologists Serial Designation F.O. 39(T). These are described. The results obtained by either method for a given fuel on a suitable engine does not differ more than ±2 cetane numbers. The cetane number should be reported to the nearest even integer.

Calibration of I.P.T. Diesel Reference Fuels H.I.Q. and L.I.Q. in Terms of Cetane and Cetene Numbers. *Jour. Inst. Pet. Tech.* **24** (1938), pp. 170-5.

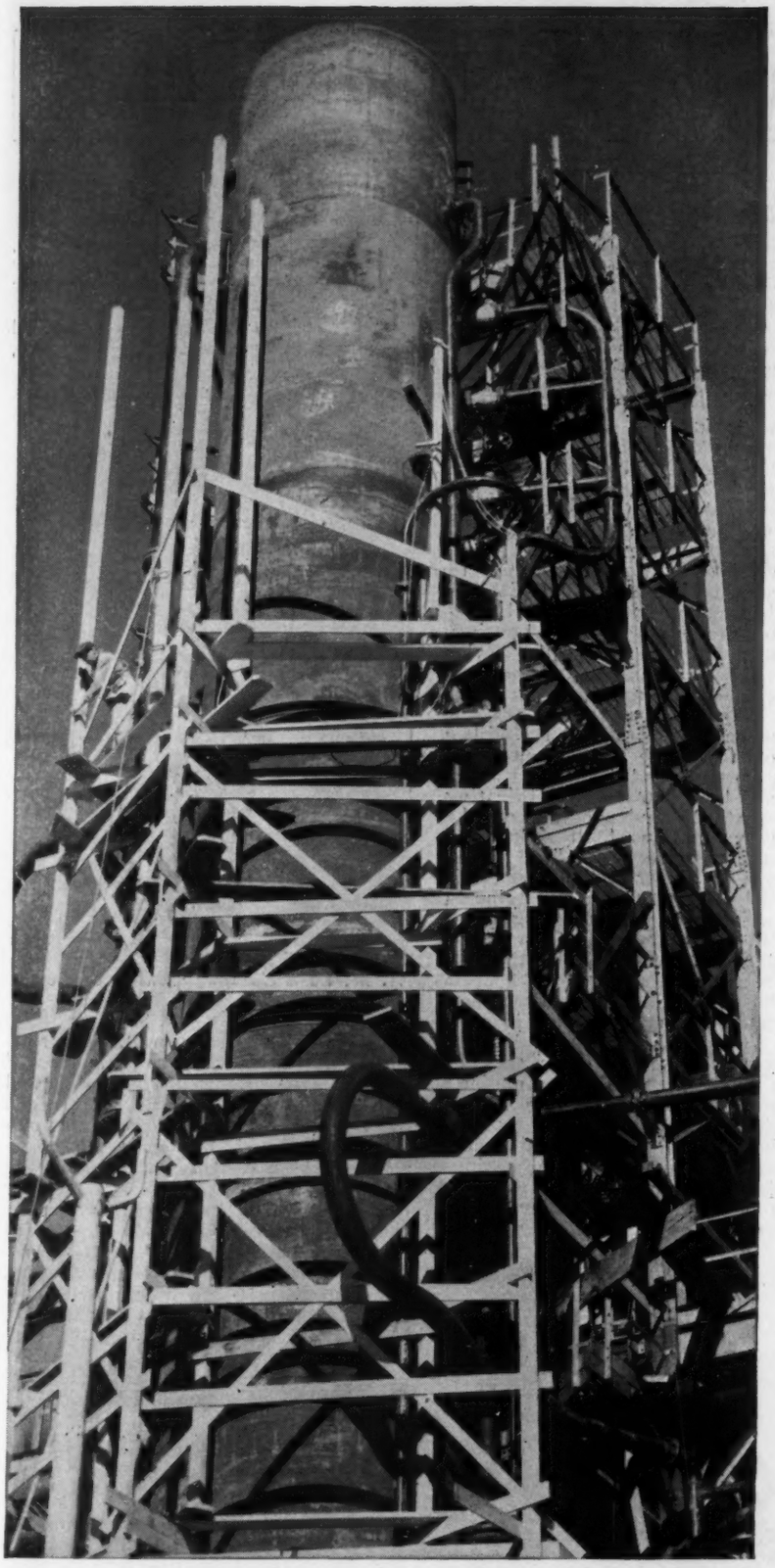
Secondary reference fuels are to be preferred to primary standards in the routine testing of diesel fuels for ignition quality for two reasons. The high cost of primary standards makes their use impracticable. Secondly, the use of such primary standards as cetene, cetane, and -methylnaphthalene involve additional experimental error, since they are not typical of normal fuels in regard to specific gravity, viscosity, and other properties, and, under some conditions of engine operation, lead to peculiarities in the timing and manner of opening of the fuel valve. It is the opinion of the I.P.T. Diesel Panel that the adoption of common secondary reference fuels will lead to a closer agreement of results between laboratories. The paper reports tests by several laboratories of High-Ignition-Quality and Low-Ignition-Quality Reference Fuels. The cetane number of the high fuel was 70½ and of the low 18; calibration was a straight line. The cetene number of the first was 80½ and of the second 20½, and the calibration a straight line. The cetane number-cetene number relationship is a straight line from the origin passing through the 80 cetene number = 70 cetane number. All of the tests indicate that the maximum experimental error to be expected on a suitable engine test is plus or minus 2 cetane numbers.

Epilating Action of Ethyl Gasoline. H. J. Templeton, George Michael and J. M. Key, *Arch. Dermatol. Syphitol.*, **37** (1938), pp. 35-42.

Ethyl gasoline containing 0.03% tetraethyl lead and 0.02% $C_2H_4Br_2$ applied to the skin of rats, guinea pigs or rabbits caused local loss of hair. Use of a gasoline containing higher concentrations of lead, for a period of a week, caused death in the case of ¼ of the animals. A case of alopecia areata totalis in an automobile mechanic appeared to be caused by vapors of ethyl gasoline, although it is admitted that no similar case has been reported.

Detection of Lead Derived From Lead Tetra-ethyl. H. Siebeneck, *Oel u. Kohle* **13** (1937), p. 1193.

The use of a 1% solution of dimercaptol-thiodiazol is recommended for the detection of lead in waste water from ethylizing plants. When lead is present in as small quantity as 3 mgm./litre a yellow precipitate is obtained. The reaction is applicable to the detection of lead in hydrocarbons. The reagent was also used to show that lead tetra-ethyl may volatilize together with hydrocarbon vapours at about air temperature.



LINCOLN "SHIELD-ARC" WELDING cuts refinery construction costs 15% to 25%

You can cut the installation costs of towers, piping, structures and tanks with Lincoln *"Shield-Arc"* welding because less steel tonnage is required, layout and fabrication are simplified and erection time is shortened. Users report savings of 15% to 25% with this construction.

The success of this improved refinery construction is due largely to the simplified welding afforded by Lincoln "Fleetweld 5." This shielded arc electrode produces welds in any position—downhand, vertical or overhead—and gives strength and ductility equal or superior to mild rolled steel. It is preferred by welders the world over.

Specify shielded arc welding; use "Fleetweld" and the new 6-in-1 *"Shield-Arc"* Welder and you will save thousands of dollars annually in construction and maintenance costs. Mail the coupon for a valuable guide to lower costs.

LARGEST MANUFACTURERS OF ARC WELDING EQUIPMENT IN THE WORLD

LINCOLN

THE LINCOLN ELECTRIC COMPANY
Dept. M-495, Cleveland, Ohio

I'd like to know how to cut refinery welding costs.
☐ Send me free Welding Procedure Guide.

Name _____ Position _____

Company _____

Address _____

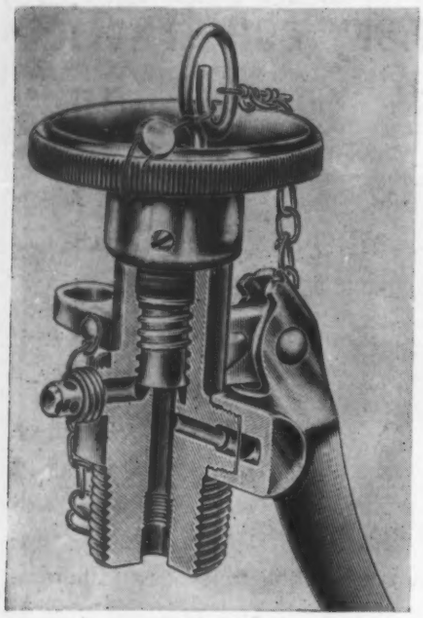
City _____ State _____

New Equipment for the Modern Plant

Extinguisher

WALTER KIDDE & COMPANY

Walter Kidde & Company, 140 Cedar Street, New York, has developed a new type hand wheel of the Lux fire extinguisher. It is a definite improvement in the design of the control wheel on the operating valve of seat type extinguishers. This new hand wheel gives a better grip, more leverage and is, therefore, easier to operate. It is provided with a pull-out pin which is kept in tension at all times assuring positive sealing. With this Lux seat type valve premature operation due to vibration is impossible.



Kidde Control

Compressor

THE COOPER-BESSEMER CORPORATION

The Cooper-Bessemer Corporation, Mt. Vernon, Ohio, recently announced the new Cooper-Bessemer Type G-MS Compressor Unit. Rated 40- to 50-horsepower at conservative speeds, this addition to the company's complete line of gas and Diesel engines and compressors is a combination of the well-known Type G-SD vertical pumping engine and a vertical compressor cylinder.

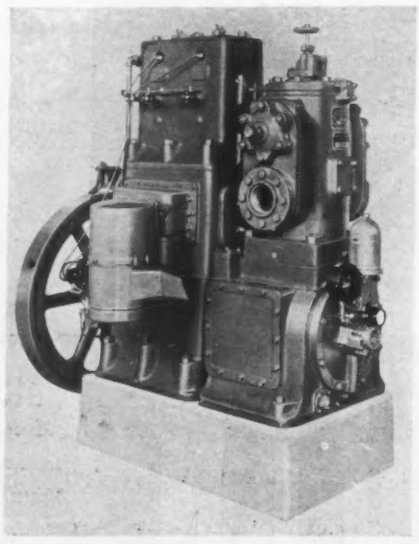
Merged with all the attributes of the G-SD vertical engine are the advantages of a 40- to 50-horsepower compressor that requires less than half the space of its horizontal predecessors, retains all of their slow-speed, long-life qualities and effects economies from first cost to actual operating and maintenance expense.

Designed for delivering gas into high-pressure lines, compressing air and refrigeration gases, re-pressuring oil sands and for natural gasoline extraction in small plants, the Type G-MS compressor is light weight, rugged and extremely compact. Easily transported, requiring a minimum amount of floor space and housing, and convertible for oil or gas fuel, the compressor can be arranged for two-stage operation through the addition of a second compressor cylinder mounted horizontally on either side of the compressor base.

The engine is a crosshead type with tapered roller bearings for its main shaft and is fully pressure lubricated. It's crankpin bearings are precision removable shells and wrist pins are the patented "T" type, providing greater bearing surfaces than is usual in this type of engine. Crosshead pin bearings are removable bronze bushings.

The vertical compressor, bolted to the drive end of a standard G-SD engine and using the same bolt circle provided for the engine clutch housing, becomes an integral part of the power unit, its husky crankshaft supported at the outer end by a radial type roller bearing. The single-acting compressor cylinders can be arranged for either single or two-stage compression, by using a vertical and horizontal combination. The compressor lubricating system, entirely independent of the engine's system, has built-in lube oil filter with the compressor base acting as a sump. Its water cooling system is in parallel with that of the engine, a single safety device guarding both against low water supply. Compressor connecting rods are identical with those of the engine and piston pins float in removable bearings. The vertical compressor cylinders are available in sizes from 6 to 9 inches. Horizontal cylinders for two-stage operation may be used in any size within the engine's horsepower rating.

Built-in centrifugal water pump, heavy-duty roller bearings, advanced-type crossheads and all iron castings of Meehanite Metal are other features of this new Cooper-Bessemer compressor unit.



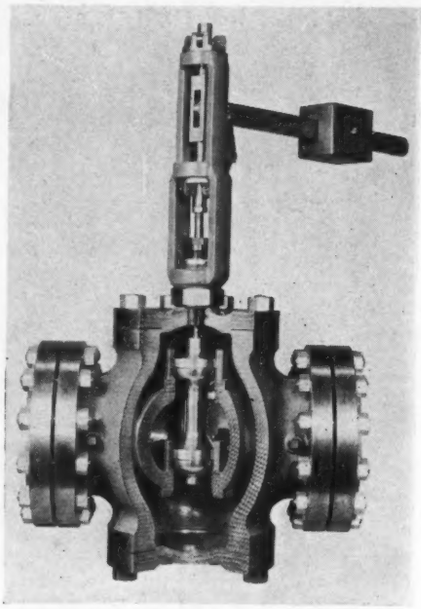
Cooper-Bessemer Type G-MS Compressor Unit.

Balanced Lever Valves

A. W. CASH COMPANY

A. W. Cash Company, Decatur, Illinois, announces the Series 42 Balanced Lever Valves for use with steam, air, oil, water (hot or cold) and most gases.

In the Series 42 valves the roller-guided top works insure free valve movement, perfect valve stem alignment, tight seating, longer packing life, and minimum of friction. The valve stem roller is guided at top and bottom. Nitralloy rollers and roller pins are used. There is no lost motion. Double or single seat. Hefty renewable seat rings. Weighty walls. Uniformity throughout and precision machined. Any type inner valve: (1) parabolic type; (2) flat type with bevel seat; (3) V-port type with bevel seat; and (4) V-port type non-seating. Large capacity. Available any size, any materials, ½" to 3" screwed ends; 1" to 12" flanged ends (any type). When used with Series 90 or Series 100 Controllers, they control, automatically, inflow or outflow (reduction, relief, differential pressure, rate of flow, liquid level).



A. W. Cash Company Balanced Lever Valve

Pillar Jib-Crane

THE HARNISCHFEGER CORPORATION

The Harnischfeger Corporation, Milwaukee, has recently developed a new self-supporting pillar jib-crane for work in side bays, low headroom areas, and other confined spaces where overhead traveling or hoist service is not available or practical. A strongly-built, well-balanced unit with jib-arm swinging on the finest roller bearings, this jib-crane is built in capacities up to 5 tons, heights up to 20 feet and to a maximum radius of 20 feet. It is practical for use throughout the industry in all types of production plants where materials are lifted, lowered or moved in the process of manufacture. Several are

for the major part, from engineers like yourself. Armed with this manual of *many* minds, Scovill representatives work with you to get results.

FOR several years Scovill deliberated over one process of making condenser tubes before being entirely satisfied with it . . . entirely certain every step could be checked from start to finish. That process was *extrusion* and followed *hot piercing* and *cup drawing*. All three methods (as Scovill fashions them) are as closely controlled as modern science and human ingenuity can make them. For example, each heat is analyzed for composition – accuracy of temperature control is maintained throughout operations — frequent inspections are made during the process — and a final check makes certain that material meets specifications.

We like to call that — engineering in production. This is supported by years of field experience. Broadly expressed in our Heat Exchange Tube Manual are conclusions formed from these years of experience . . . information collected,

Not only on immediate problems is the Heat Exchange Tube Manual used; its 149 weighty pages are also at the disposal of Scovill customers and prospects.

Yes, we sell condenser tubes in eleven different alloys, but in addition, we provide Engineering data, Engineering production, and an Engineering service to each Scovill customer.

On request we will send an illustrated booklet describing the three methods by which Scovill makes condenser tubes. Address Scovill Manufacturing Company, 15 Mill Street, Waterbury, Connecticut.

Tubes in an oil refinery heat exchanger had an average life of 11 months. This was normal for the equipment under existing conditions but was not so satisfactory as to preclude consideration of other tube alloys. Scovill engineers suggested the trial of tubes of a different composition. This was done and, although the cost of the recommended material was 32% greater than the alloy previously used, tube life was lengthened to 2 years, an increase of 118%, in addition to the usual savings made from longer tube life.

SCOVILL
Masters of Metal

Scovill Condenser Tubes

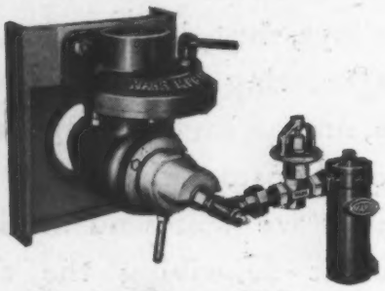
one product . . . three services

already in use throughout the country. This type of crane may be furnished with either the standard P&H pendant rope of push-button controls on the hoist and, for slightly higher cost, may be equipped with the newly-presented P&H Push-button Master Variable Speed Controller which controls all lifting, lowering and traveling operations. Operators report that the boom swings with ease and that it is a great aid in speeding up production. Installation is made without the need of any revamping of existing supports.

Oil Burners

MAHR MANUFACTURING COMPANY

Mahr Manufacturing Company, Division of Diamond Iron Works, Minneapolis, Minnesota, announces a complete new line of low-pressure triple-atomizing oil burners, known as the "20" series. The burners are designed for use in industrial heating operations and are of rugged design to withstand severe service. All parts are accurately machined to insure uniform operation of all burners of the same size and to insure ease of parts replacement.



Mahr Low-Pressure Oil Burner

The burners are easy to light even with the heavier grades of oil and a cold furnace. They are free from oil drip and carbonizing in the heat duct. The air control is by a lever handle on the internal unit. The oil supply is controlled by a type "G" oil regulating valve. For burning low-pressure gas, a special gas internal unit is installed in place of the old internal unit. All parts are interchangeable and can be changed from one fuel to the other in a few minutes.

Ratchet Wrench

BONNEY FORGE & TOOL WORKS

The Bonney Forge & Tool Works, Allentown, Pa., announces that a 15-inch Ratchet Wrench has been added to its line to meet an increasing demand for a ratchet of that length for use with ½-inch square drive sockets and handles and attachments.

Known as No. 4098, it is of the reversible type. A feature of the wrench is that it can quickly be changed into a 10-inch ratchet for use in close quarters by simply removing the extension which screws deep into the handle of the 10-inch end. The knurled double grip permits the maximum leverage to be exerted.

It is drop-forged of Zenel steel, is chrome-plated and buffed to a high, permanent lustre.

The tool, the manufacturer claims, is highly desirable to mechanics because it offers all the advantages of both 10-inch and 15-inch ratchets in a single tool at only slightly increased cost over the 10-inch size.

Vertical Welder

THE HARNSCHFEGER CORPORATION

The Harnischfeger Corporation, Milwaukee announces a 150-ampere vertical type welder. Designed to occupy a minimum of floor space, this new welder is a highly adaptable machine, available for a wide range of work in welding the lighter gauge metals, both ferrous and non-ferrous. With plug-in type cable receptacles for easy current reversing, and patented, single-current control, it is simple in operation. It is designed for high current uniformity, and is an ideal unit for use in the production welding line where smooth, uniform welds are essential. Furnished in the A.C. drive only, this little machine is less than 4 feet in overall height. An ingenious towing handle provides easy movement around the shop, and ample stability when raised to form a 3-point base. Proper ventilation and cooling is provided through the fresh air intake at the top, and the exhaust at the bottom. It can also be furnished with lifting ring and without wheels where portability is not necessary.

Ignition Lag Indicator

AMERICAN INSTRUMENT COMPANY

The American Instrument Company, Silver Spring, Maryland, recently introduced the Aminco-Penn State Ignition Lag Indicator for accurate and speedy determination of the ignition quality or cetane number of Diesel-engine fuels. The inherent accuracy of the instrument in rating Diesel fuels is greater than one fourth cetane number, and with it, the ignition quality of from 10 to 15 fuels per hour have been determined in actual practice; thus it is more reliable than the bouncing-pin method and about ten times faster.

This indicator, which is supplied to fit the standard Waukesha C.F.R. Diesel Test Engine, can be installed in about one hour by the average operator, and with it, any person qualified to operate the test engine can readily grasp the method of conducting satisfactory tests.

The method consists of injecting the fuel at a given time before top center, and adjusting the compression ratio to give ignition at top center, as measured by the indicator. The fuel whose ignition quality is known is bracketed between two known fuels.

The apparatus consists of magnetic pick-ups for detecting the injection and ignition impulses, a double thyratron relay for converting these impulses into short-lived surges of electricity, and a neon protractor mounted on the flywheel and bearing two neon lamps (set at a known angular distance from each other) to convert the impulses into a visual signal. The apparatus is described in manufacturer's Bulletin 1090-RN which will be sent on request.

Air-Actuated Remote Recorder

METRIC METAL WORKS

Metric Metal Works, Erie, Pa., of American Meter Company, announces completion of field installation tests on its perfected new "Metric" Air-Actuated Remote Recorder.

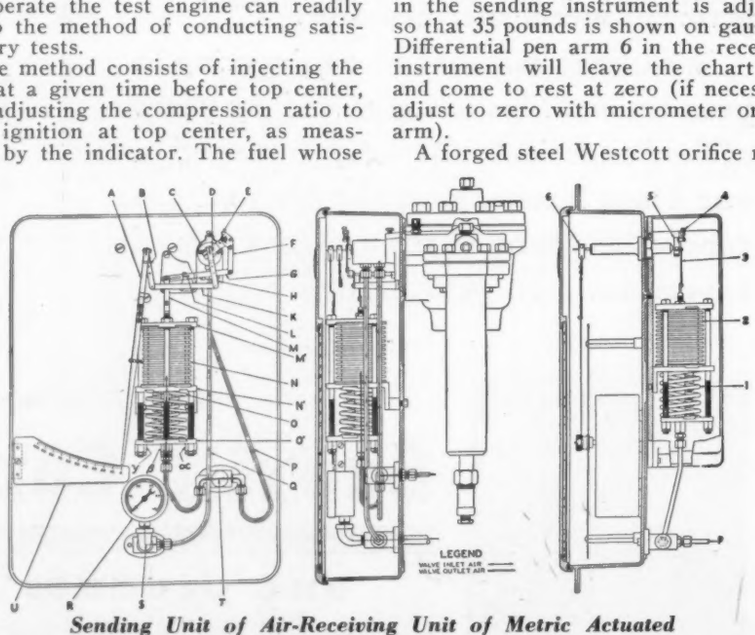
This remote recorder accurately charts—at a point remote from meter installation—the volume of gas, air, steam or fluid measured by orifice method. The device consists of sending, receiving and control apparatus—and the control mechanism may be installed in either the sending or receiving unit case.

(This same principle of remote transmission may be utilized in connection with zero to 100 percent throttling—in the control of rate-volume, or for automatic reset control.)

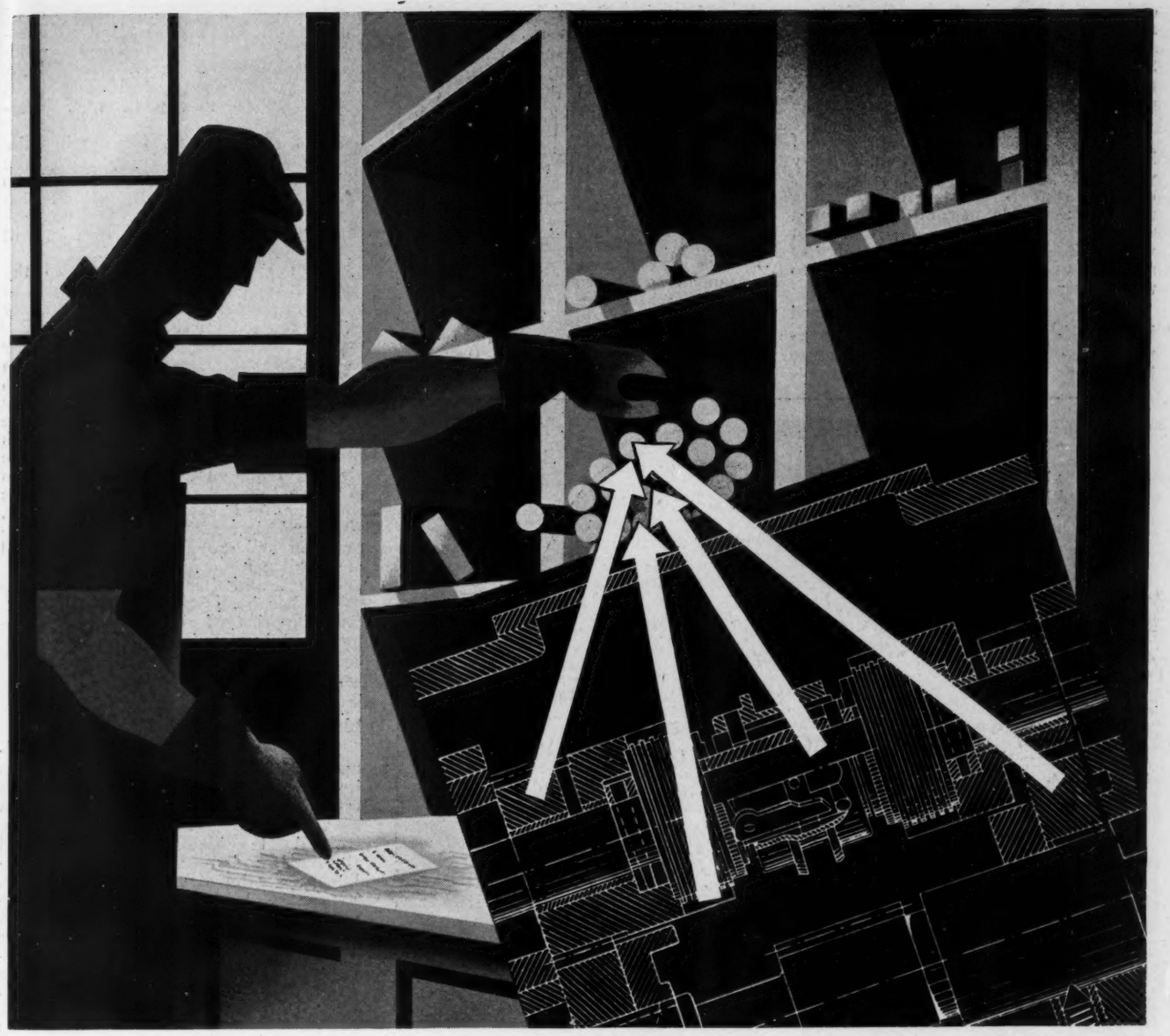
Position of differential pen arm in the sending of the Remote Recorder is at all times duplicated in the receiving unit by the position of the differential pen arm which makes the chart record, and there is little lag in synchronization. Sending and receiving units are connected by 3/16-inch copper tubing. To put the Remote Recorder into service, it is necessary only to set the differential pen arm at zero on the chart, and to open an air-line valve and adjust a pressure-reducing valve. Operation is positive.

Valve in the air line, connected at S, is opened; and pressure reducing valve in the sending instrument is adjusted so that 35 pounds is shown on gauge R. Differential pen arm 6 in the receiving instrument will leave the chart hub and come to rest at zero (if necessary, adjust to zero with micrometer on pen arm).

A forged steel Westcott orifice meter



Sending Unit of Air-Receiving Unit of Metric Actuated Remote Recorder.



MANY PARTS . . . ONE STEEL

SPECIALIZATION has its spheres, but in a manufacturing material ***versatility*** usually has the advantage. For instance, a truly versatile steel—one that can be made to meet the individual requirements of different applications—offers economies and shop efficiencies obviously impossible with a multiplicity of types.

One company building machine-shop equipment has standardized on a Chrome-Manganese-Moly steel for a great variety of parts. It was selected because it can be heat treated to a high hardness and still remain readily machinable.

Versatility is a feature of Moly steels in general. It reduces the chances of error by simplifying stockroom procedure and inventories; permits greater standardization of processes; assures more uniform results; and is an important factor toward economy.

The wide range of applications of Moly steels has been definitely proved in laboratory, shop and field. Our book, "Molybdenum in Steel," offers a quick technical survey of their scope. We invite engineers and production executives to write for it. Climax Molybdenum Company, 500 Fifth Avenue, New York City.

PRODUCERS OF FERRO-MOLYBDENUM, CALCIUM MOLYBDATE AND MOLYBDENUM TRIOXIDE

Climax Mo-lyb-den-um Company

MOLY

differential gauge in the sending instrument actuates differential pen arm A and lever B. Pen Arm A indicates on Scale U the differential across the orifice plate at each instant. Lever B, through link K and lever H, moves the valve of a standard Metric Rotary Pilot (C)—Consisting essentially of housing sleeve, rotary seat and rotary valve. Air supply for pilot valve C is connected at S. Gauge R, indicating pressure available, is connected to pilot valve C by line Q. The outlet of pilot valve C is line P, which is connected to sylphon, and a point T is connected to the receiving instrument.

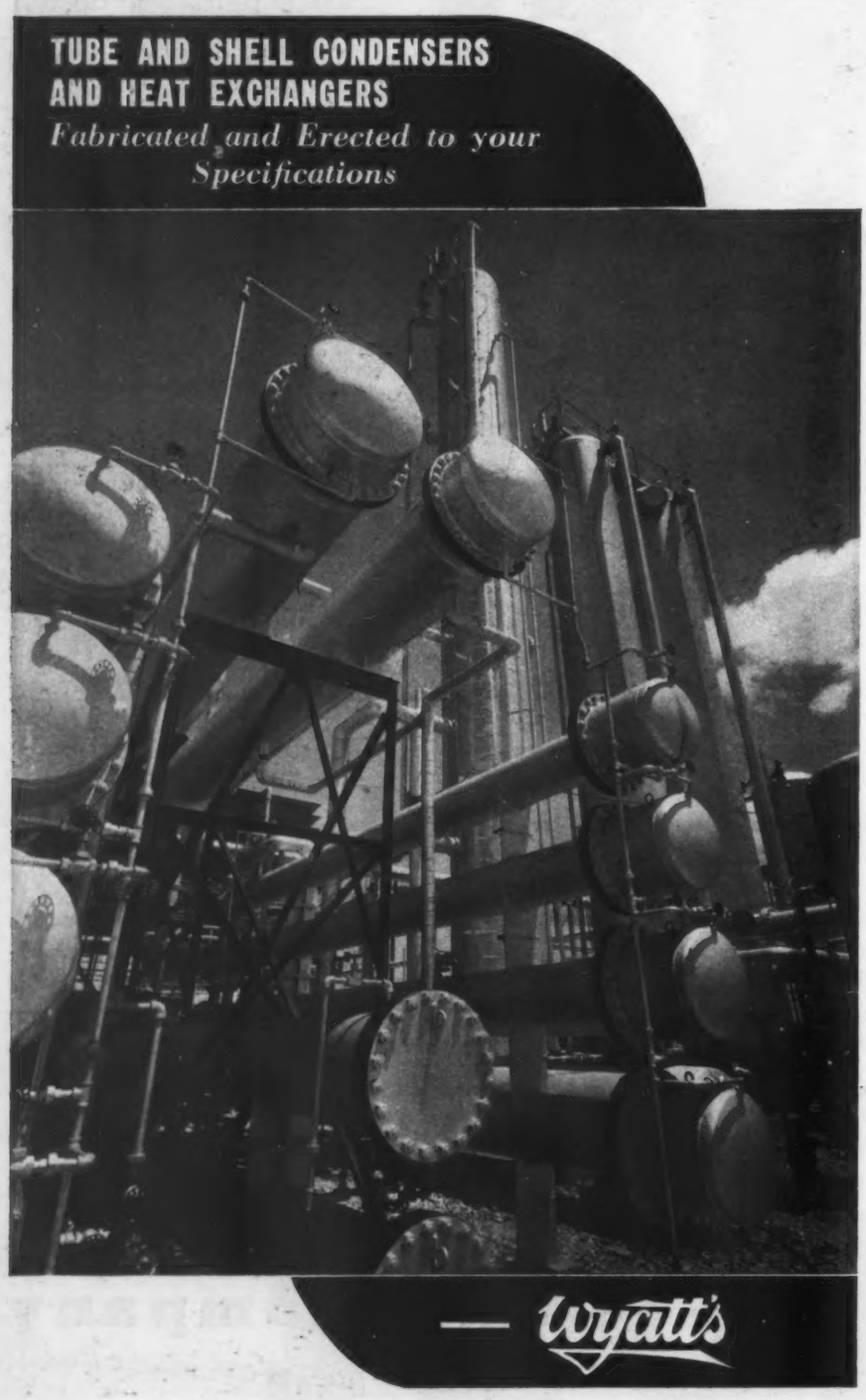
If differential pen arm A is moved in a clockwise direction, lever H moves the valve of pilot C, increasing pressure in outlet pipe P. Line P extends through spring O and is connected to sylphon N at bracket N′. Pressure increase in line P causes spring loaded sylphon N to expand, M′ and O′ to rise, and spring O then to be compressed. Link M moves lever G (pivoted at L) clockwise, and this movement through link F, adjustment E and lever D, moves clockwise the seat of the pilot.

It is seen that the valve of the Metric Pilot is moved by the differential pen arm, and the seat of the pilot valve is moved in the same direction by the expansion of the sylphon N. Consequently, when the seat of the pilot valve moves through the same angle as the valve, there will be no further increase in pressure in line P. For a definite movement of the pen arm, there will be a definite expansion of the sylphon N to permit a definite pressure in line P, and to produce definite compression in spring O. Therefore, a definite pressure in the outlet line P will be obtained for each position of differential arm A.

The force available for moving the pilot valve seat and compressing the spring for a full scale deflection, is 30 pounds. Since practically all of this pressure is utilized in compressing the spring, a small change in friction will not produce any inaccuracy.

Outlet line P is connected to the receiving instrument, which consists of a spring loaded sylphon 1-2 (exactly similar to sylphon N-O). Sylphon 1-2—through link 3 adjustment 4 and lever 5—actuates pen arm 6. As there is a definite position of sylphon 1-2 for each pressure in line P, just as there is for sylphon N-O, pen arm 6 will assume a definite position on the chart for each definite position of pen arm A in the sending instrument—and the positions of these two pen arms always will be the same. As in the sending instrument, 30 pounds is available for spring compression and movement of the control mechanism for a full scale deflection.

Accuracy of this long distance transmitter has been verified during an extended period of rigorous test in various field installations.



Floor Truck

LEWIS-SHEPARD COMPANY

Lewis-Shepard Company, 245 Walnut Street, Watertown, Mass., presents its newly-designed floor truck. This truck has many exclusive features, such as arc-welded frame of special design with double side girders, which hold the hardwood top in place with a vise-like grip, eliminating the use of bolts. T-type steel end protection saves top wood from being chewed through rough usage. Casters are hung on four steel arch sections which, by their ingenious arrangement, allow a large kick space. The main wheels are suspended on a bridge type hanger. Axles are easily removable and are reinforced by means of a tubular axle housing. Hyatt roller bearings are used in all wheels.

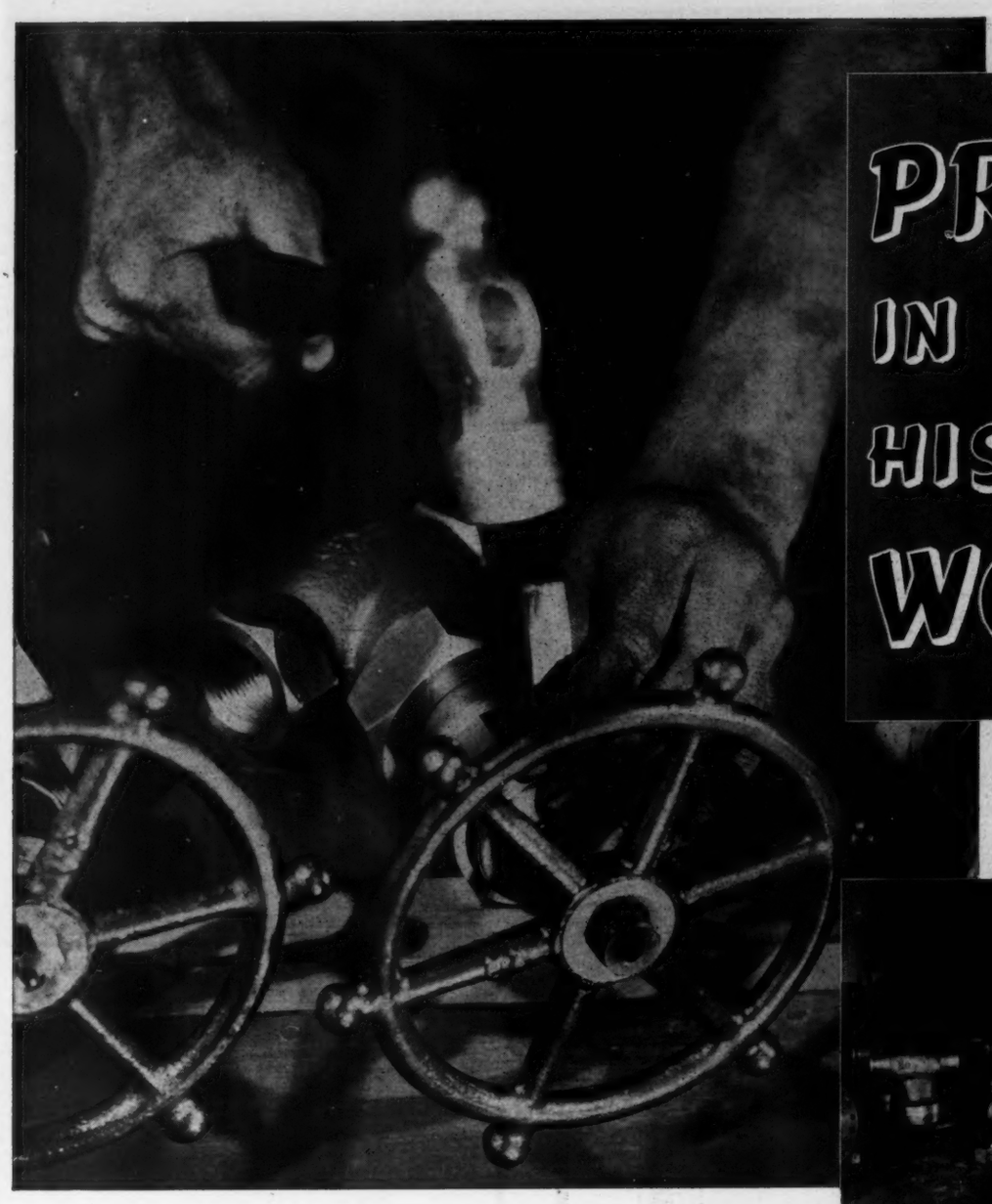
Much thought was given to weight distribution, and the design allows easy steering and rolling, with a minimum amount of end tipping. Metal, solid rubber or pneumatic tires are available. Standard capacities are from 1000 to 4000 pounds.

Desuperheater

NORTHERN EQUIPMENT COMPANY

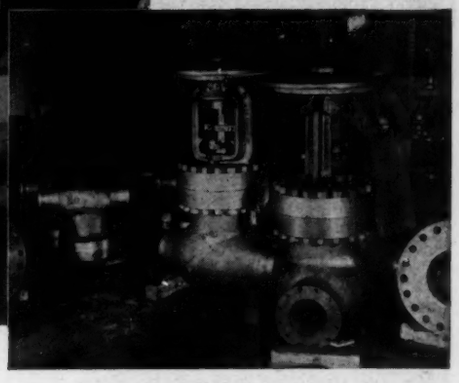
Northern Equipment Company, Erie, Pennsylvania, has introduced the new Copes Desuperheater. It is designed for either total or partial elimination of the superheat from steam to be used for process work, or for auxiliaries built for reduced-temperature steam. It operates on steam from 212 to 1100° F., maintaining within close limits the desuperheated steam temperature, regardless of changes in temperature of the superheated steam.

The Copes Desuperheater is installed in the steam line as a self-contained unit. The only connections needed are a water supply for desuperheating, a water or air pressure line for the



PRIDE IN HIS WORK

Edward workmen put the best they have into every Edward valve, be it big or little



ASK an Edward assembler whether Edward valves are good! He'll tell you. When he stamps his symbol on a valve, he knows it has qualities — plus values in every detail — other valves don't have. He has pride in his work because he is proud of the Edward name — a name associated with brilliant performance ever since the earliest use of high pressures.

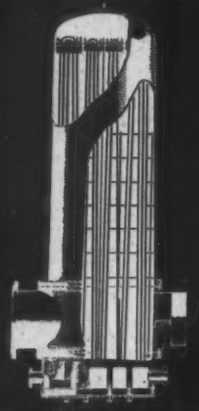
And remember — today's Edward valves get by on no worn-out reputation. By gruelling tests, intensive field study and technical research, they are being built ever better. Find out about them!

• • •

The Edward Valve & Mfg. Co., Inc.
EAST CHICAGO INDIANA

EDWARD VALVES

LEACH
FRACTO
CONDENSERS
for High Pressure
and Temperature.



Also Heat Exchangers for Vacuum and Atmospheric Service.

Fracto Control

Patented in the United States and Foreign Countries.

C. H. LEACH CO., Inc.
117 Liberty Street, New York, N. Y.

"Bill says"

For Safety Specify KERLOW FLOORS

KERLOW gratings and safety steps are made in all riveted and rectangular types and cut to fit your exact requirements.

For: Subways, boiler room floors, walkways, fire escapes, platforms, areaways, sidewalks, trench covers. KERLOW Bridge Paving (open and solid types).

Ask about **Kerlow "BOLDEI" Safety Steps.** —The latest advancement in safety steps.

KERLOW
GRATING PRODUCTS

Non-Slipping

Write for Catalog
Representatives in Principal Cities

KERLOW STEEL FLOORING CO.
Dept. R
210 Culver Ave. Jersey City, N. J.

diaphragm operator, and a drain to carry off excess condensate brought over by the steam when the desuperheater is first cut into service.

The flow of cooling water is controlled at the spray nozzle. A constant pressure drop is maintained across the nozzle, permitting a continuous supply of cooling water to be sprayed into the superheated steam in exact proportion to the demands, from minimum to maximum flows. This fact, plus the positive action of the thermostatic temperature control element, assures dependable operation and sensitive control under all conditions.

Boiler feed water can be used as a cooling water supply. Air or water can be used to actuate the pilot operator of the water control valve. The desuperheater can be designed to use the cooling water for this purpose if desired.

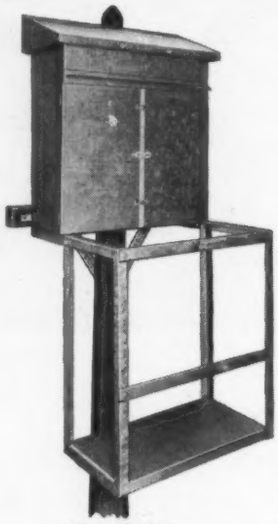
Simple external adjustments permit varying the degree of desuperheat and the sensitivity of control at will.

Transformer Housing

FRANK ADAM ELECTRIC COMPANY

Frank Adam Electric Company, St. Louis, Missouri, has developed a new pole-mounting weatherproof cabinet, for outdoor meter and transformer housing.

The cabinet proper is made to house meters or transformers—or both. It is weatherproof—sturdily designed—rigidly built—and provided with 2 substantial doors that fit snugly against gaskets to assure tight seal when the doors are closed.



Frank Adam Transformer Housing.

Internally, the cabinet is fitted with ⅞-inch cypress instrument mounting board—also adjustable mounting straps to accommodate several styles and sizes of transformers.

Screened openings for ventilating are provided under the hood at the top of the cabinets. Water cannot enter through the ventilating openings.

The cabinet can be furnished with or without the platform stand shown in the photograph—the latter being especially convenient for workmen's use when mounting and servicing the housed equipment.

All parts of the entire construction are of heavy metal, substantially constructed to withstand severe outdoor service.

Testing Cabinet

GENERAL REFRIGERATION CORPORATION

General Refrigeration Corporation, Beloit, Wisconsin, has developed a special testing cabinet for use in the method of testing for the cloud and pour points of lubricating oil. During the past year a number of these test cabinets have been used by some of the larger refining companies in testing laboratories. Among the advantages claimed for this cabinet is its compactness, the accuracy and constancy of the temperatures maintained and the speed with which cloud and pour tests can be conducted through its use.

General Refrigeration Corporation Testing Cabinet.

The cabinet is 36″ long, 36″ high and 22″ deep, heavily insulated with corkboard, with black enamel finish and stainless steel top and trim. A ½ H.P. water-cooled Lipman refrigerating machine connected to a full-flooded annular type lowside is installed in the base of the cabinet, making the entire equipment self-contained in every respect. Power and water supply and drain lines only, need be run to the cabinet.

The cabinet has three compartments with openings in the top, one for each of the three temperatures at which cloud and pour tests are made. Each compartment has six 2″ I.D. wells or jackets conforming to A.S.T.M. specifications, holding standard cylindrical oil test bottles giving the cabinet a total capacity of 18 test bottles.

Temperatures in each compartment are regulated by constant pressure regulating valves conveniently located, one for each compartment. Once set at the proper point, temperatures are maintained automatically and the operator wastes no time in making adjustments. Temperature in the first compartment is maintained at 30 to 35° F., in the second compartment at 0 to plus 5° F., and in the third compart-

WANTED—Chemist having five or more years experience in charge of asphalt manufacture, corrosion control, treating, boiler feed water control, research and shipments. Must have technical education as well as practical training and ability to organize this department. State salary desired. Box 50, The Refiner, Houston, Texas.

INSULAG

Reg. in U. S. Pat. Off.

—a Refractory Lagging for Temperatures up to 2200°F.

With Remarkable Insulating Properties

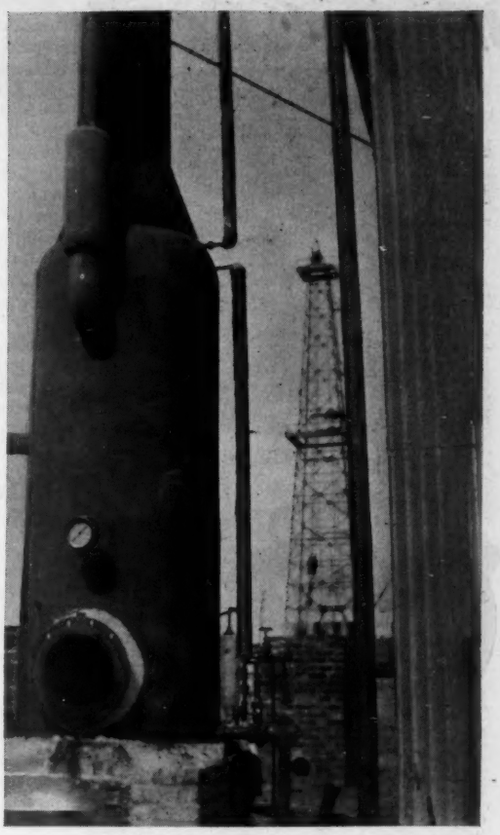
INSULAG is light weight—sets quickly—adheres to hot or cold surfaces—expands after application and retains volume—no shrinkage, cracks, pulling away, or powdering off—develops high mechanical strength—withstands shock, abrasion and vibration—durable—defies weather—does not lose insulating value after repeated heating.

Usual practice is to trowel on metal lath. Makes a white, hard-finish surface, weather-proof, air-tight, and free from cracks.

Shipped in powdered form. Mixed with water on the job to a heavy troweling consistency. ***Send for New Bulletin 327R***

QUIGLEY COMPANY, INC.
56 W. 45 ST., NEW YORK, N. Y.

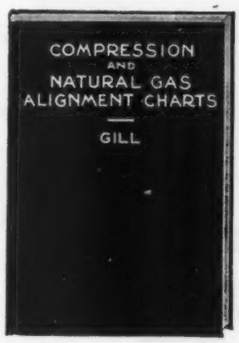
Distributors with Stocks and Service in Important Industrial Centers Throughout the United States, Canada, and in 32 Other Countries.
In Canada, Quigley Company of Canada, Limited, Lachine, P. Q.



Tube Still INSULAGGED

COMPRESSION AND NATURAL GAS ALIGNMENT CHARTS

By THOMAS T. GILL



The charts in this book have been found useful in solving field problems arising in connection with the measurement, compression and transmission of natural gas, and in the manufacture of natural or casinghead gas. As many of the formulas in common use in natural gas operations are of an impirical nature, with constants that must be evaluated under varying conditions, it will be found that alignment charts are sufficiently accurate for nearly all purposes except for metering large quantities of gas, and here they serve as an excellent check on other calculations. Contains 41 charts, 65 problems. Price $3.50 Postpaid.

Send check to the

GULF PUBLISHING COMPANY

P. O. Box 2811

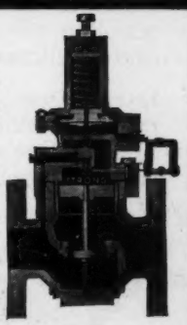
HOUSTON, · · TEXAS

PIPEWRENCH PETE SAYS:

I'M TALKIN' TO THE MAN WHO WANTS 47 POUNDS!

Or 7, or 107 pounds!

Here's one pressure regulator that isn't bad news! It's the STRONG packless, pilot-operated, single-seated valve for air, steam or gas.



Amazingly simple, and with valves and seat of "wear ever" ANUMETL, you can install a STRONG supersensitive regulator and get accurate pressure reduction *from now on*—and with practically no upkeep! Try one, and you'll standardize on STRONG!

FREE! Accurate, easy way to size pressure regulating valves. Send for Bulletin 154.

STRONG

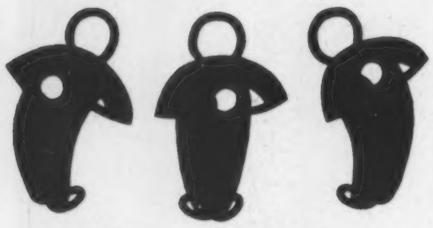
QUALITY STEAM SPECIALTIES

The Strong, Carlisle & Hammond Company
1392 West Third Street, Cleveland, Ohio

R-2

Make A Bow!

"John Crane" Style 804-D



Recommended for Highest Temperatures (1000° F.) on Hot Oil and Gasoline Service.

for

VALVE STEMS

Hot Oils — Hot Gases

The base of this packing is purest asbestos yarn—jacket over jacket construction. Each and every strand is graphitized and treated with CRANEPRENE—our own **oil and gasoline proof** binder. This produces a packing immune to hot or cold oil, gasoline, kerosene, crudes and distillates.

Easy to use — permanent packing! Manufactured in Spools, Reels and Coils. All sizes from 3/16" to 1".

Send for this new oil Bulletin.

CRANE PACKING CO.
1804 CUYLER AVE. CHICAGO, ILLINOIS

ment —30 to —25°F. Temperatures are identical in all jackets of each compartment and if desired, may be quickly changed. A thermometer well is also located in each compartment.

A push-button switch controls the starting and stopping of the refrigerating machine and a pilot light indicates whether or not the machine is running. Safety devices such as high pressure cutouts and motor overload protection are standard equipment on the Lipman refrigerating unit. After the machine is started it takes approximately 10 minutes to secure suitable temperatures in the warmest compartment, 20 minutes in the middle compartment, and 35 minutes in the coldest compartment. A cabinet of this type is of real assistance in the successful operation of a general laboratory or gasoline and lubricating oil refinery laboratories.

Safety Valve

J. E. LONERGAN COMPANY

J. E. Lonergan Company, 211 Race Street, Philadelphia, announces an improved safety valve designated as model "WTN" in which, the manufacturer states, have been incorporated all of the best features developed during many years of manufacture of such devices. It is as simple and practical as can be made and yet give a high lift and large capacity, it is said. The valve has an advantage in that it has a full throat tube seat area which will induce a high capacity and cause no restriction of the flow. This is accomplished without the necessity of an excessive lift which results in a tax on the spring and lessens its life. The disc is top guided, and the spring encased, placing it out of the flow of steam or hot liquids. The working parts of the valve are symmetrical in design, calculated to allow even expansion and contraction through the uniform heat transfer from one working part to another, thus relieving the abrasive or tearing action across the seat, caused by the surfaces expanding and contracting unevenly. The "WTN" valve can be manufactured from any metals suitable for its intended service and in accordance with specifications for gases or liquids of any nature. It is furnished with flanged inlet and outlet, flanged inlet and screwed outlet or screwed inlet and outlet.

Gas Indicator

DAVIS EMERGENCY EQUIPMENT COMPANY

Davis Emergency Equipment Company, 55 Van Dam Street, New York, announces a new combustible gas indicator for measuring directly the combustibility and explodibility of gas-air mixtures.

In designing this indicator, the object was to produce an instrument that would be as light, as compact, and as economical as possible without sacrifice of accuracy of measurements. The weight of the indicator, complete with batteries, is only 6 pounds; the dimensions of the instrument panel are 6¾ x 5⅜ inches; and the depth of the case is 3¾ inches. The instrument is, therefore, easy to handle and carry around.

Current is supplied by two standard dry batteries, thus obviating the difficulty of obtaining special batteries. Two batteries give 3½ hours of continuous operation, and, when used intermittently, as is usually the case, they permit a large number of tests to be made before renewal is required.

The resistance of the platinum filaments used in both the active and comparison cells is controlled within very close limits, which insures the same accuracy found in larger instruments. The two filaments are interchangeable, making maintenance more convenient.

A rugged 3-inch meter shows directly the percentage of the lower explosive limit of the mixture being sampled. The meter is mounted under the panel, with only the scale showing, and is protected from damage by shatter-proof glass. A push button changes the meter reading to volts for checking purposes, and the change can be made while sampling.

The Davis combustible gas indicator is used for measuring the flammability of the atmosphere in tanks and other containers of flammable liquids and gases, ship holds, manholes, conduit systems, and other places where flammable gas-air mixtures may be found. A test can be made in a few seconds and guards against the danger of introducing flames or sparks or doing welding and other "hot" work in flammable or explosive atmospheres.

Portable Cooling Unit

AMERICAN INSTRUMENT COMPANY

American Instrument Company, Silver Springs, Maryland, announces a new portable cooling unit for use in baths or tanks where bath temperature is to be maintained at or below room temperature with an accuracy of plus-

NEWARK

Discriminating refiners the world over have learned that when they specify "NEWARK" Wire Cloth Products, they are getting the utmost in value — Wire Cloth in all metals, weaves, meshes and sizes; Testing Sieves; Shakers; Riddles; Metallic Filter Cloth; Strainers; Sifters, etc. That is why they say

"I always insist on Newark Wire Cloth"

NEWARK WIRE CLOTH CO.
350-364 Verona Ave. Newark, N. J.
Sales Representatives: Chicago, Detroit, Havana, Houston, Los Angeles, San Francisco, Tulsa

TUBE CLEANERS

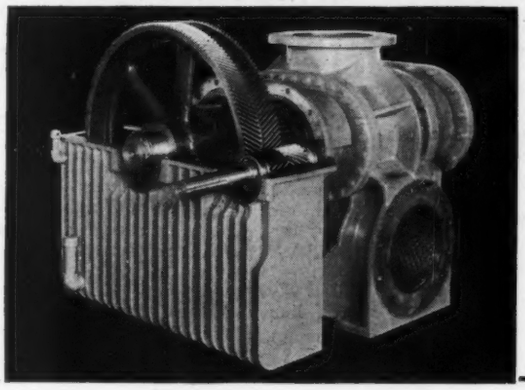
FAMOUS FOR SPEED-POWER ENDURANCE

See Our Adv. in SWEET'S

The ROTO Company

145 Sussex Ave., Newark, N. J.

Clean SMALL TUBES Faster-Better with a ROTO JUNIOR



INTEGRAL GEAR REDUCTION

FOR COMPACTNESS AND LIGHT WEIGHT

Either spur or herringbone integral gear reductions are available. This construction is ideal for refinery service where size and weight are restricted. We will appreciate quoting on your requirements.

WATEROUS COMPANY

St. Paul, Minnesota

Established 1886

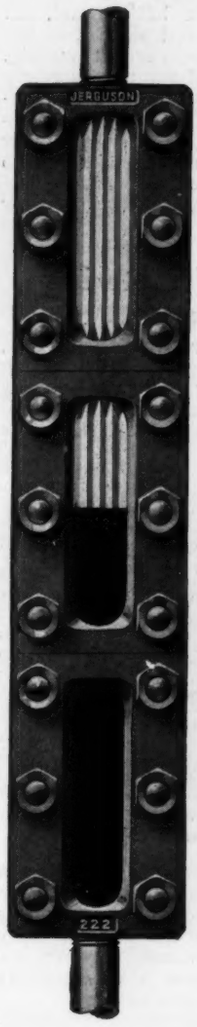
WATEROUS HEAVY DUTY ROTARY PUMPS

JERGUSON

REFLEX GAGES

Year in, year out Jerguson has served the industry, supplying these accurate, dependable gages for steam boilers and for indicating liquid levels in tanks, towers, stills, etc. Every oil man knows—

The *empty* space appears WHITE



The *liquid* shows BLACK

Safe and dependable at all temperatures and pressures. Furnished with or without valves for every type of service. Full information upon request.

JERGUSON GAGE & VALVE CO.

87 FELLSWAY

SOMERVILLE, MASS.

minus 1°C. It is especially advantageous for warm weather operation of constant-temperature baths.

The unit consists of a suitable refrigerator unit fitted with a cooling coil and expansion valve. The refrigerator is mounted in a perforated metal housing. The cooling coil is connected to the refrigerator by seamless flexible metal tubing. The expansion valve is automatic in operation and requires no attention.

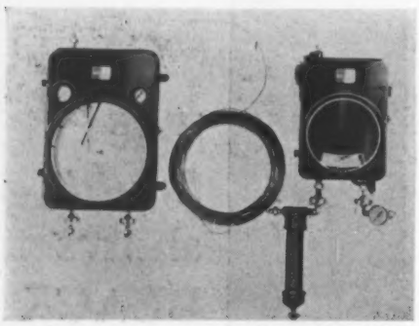
The refrigerator measures only 12x15 x21 inches high, and, being mounted on ball-bearing casters, may be moved about easily.

This unit is put into service quickly and no installation is required. Merely roll the cooling unit to the bath or tank whose contents are to be cooled, immerse the coil in the bath liquid, set the thermoregulator and place it in the bath, plug in to the current supply, throw the switch, and the unit is ready for continuous duty. No pipe connections to be made; no valves to operate; no adjustments to be made other than setting the thermoregulator; no boring of holes or breaking of pressure connections; no brine or water cooling system required.

Pneumatic Telemetering

THE BRISTOL COMPANY

The Bristol Company, Waterbury, Conn., has developed a pneumatic telemetering system for recording and automatically controlling temperature, flow, pressure and liquid level, known as Bristol's Metavane System.



Bristol Metavane System

While this telemetering system has a wide field of application in industry, it is particularly well suited for use in plants where explosive fumes are present. Being operated entirely by air under pressure, the explosion hazard present when electricity is used is completely eliminated.

Bristol's Metavane system of telemetering provides a simple, accurate method of measuring such variables as those mentioned above, at any point in a plant or process, and of transmitting the measured value pneumatically to some remote central location where it can be either recorded, indicated, or automatically controlled.

The Metavane consists of two instruments: the transmitter and the receiver. The transmitter measures the variables in question, indicates its value on a scale for the use of the operator, and transmits the reading to the receiver, which may be several hundred feet away. The two instruments are connected together by means of copper tubing. A 15 lb. air supply introduced at the transmitter provides power to the telemetering system.

▼ BUSINESS NOTES ▼

TO BETTER coordinate activities in the development and application of standards both within the company and without, General Electric Company has formed a new standards department. This organization will work with the various local, national, and international associations and agencies interested in standards and codes and will also promote the development of standards for use in the company's engineering and manufacturing department. The new department will be headed by L. F. Adams, who will serve as manager and assistant to Vice President E. O. Shreve. Associated with Adams will be E. B. Paxton, E. R. Anderson, H. W. Samson and H. W. Robb.

Formation of the standards department centers in one organization the work formerly done by smaller groups throughout the various General Electric plants. At the same time, however, the several standardizing committees already established by the company will continue to function in the development and design of apparatus in their respective lines.

THE Foxboro Company announces the change of address of its Dallas office and branch factory to 1710 North Akard Street. The entire building will be occupied by The Foxboro Company, in order to enable it to maintain a larger stock of instruments, charts and replacement parts.

THE Lincoln Electric Company, Cleveland, Ohio, announces appointment of J. M. Chapple as managing director of the new manufacturing subsidiary, Lincoln Electric Company (Australia) Pty., Ltd., recently established at Alexandria, (Sydney) Australia, by J. F. Lincoln, president of the company. A factory building has been purchased which will manufacture: arc welding machines, electrodes and accessories. Chapple will be in charge of manufacturing, sales and advertising of the new company.

THE Marley Company, Kansas City, Kansas, manufacturers of water cooling equipment, announce the opening of its southeastern sales branch in Atlanta, Georgia. T. A. Tobin, formerly of the home office sales staff, has been transferred to Atlanta and is in charge of the new offices in the Walton building.

SHEFFLER-GROSS COMPANY, Drexel Building, Philadelphia, announces appointment of Specialty Products Company, Boston, Mass., as exclusive distributors in the New England states for Duoflo suction and discharge strainers.

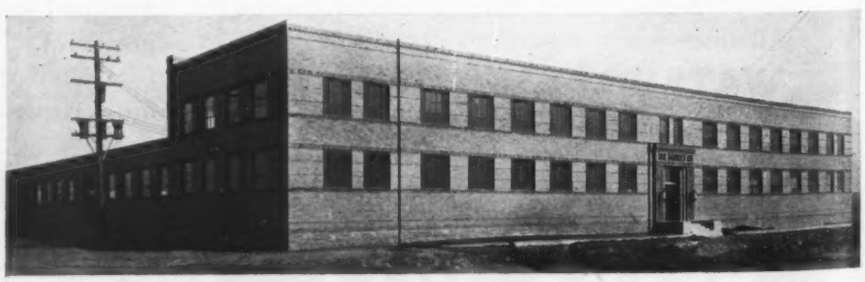
MURPHY Diesel Company, Ltd., has appointed W. C. Morgan as district sales engineer in the southwest territory to be located in Tulsa. W-K-M Company is agents in the Mid-Continent field.

MICHEAL J. LEAHY, consulting chemical and metallurgical engineer, Fort Worth, Texas, has established a new office and research laboratory at 809 Nashville Street, and has equipped the laboratory for research and development of industrial chemical and metallurgical processes and for experimental work on these types of problems which may arise in the petroleum industry. For several years Leahy has specialized in design and development of processes and equipment, in patent research and in technical aid in patent litigation. The new laboratory will be used for the testing of new processes on a semi-plant scale in which commercially obtainable metals and parts and industrial grades of raw materials will be used. Leahy has contributed several technical articles to THE REFINER and to the trade and technical press during the past several years.

J. B. WITTRUP, for 23 years connected with The Manhattan Rubber Manufacturing Division of Raybestos-Manhattan, Inc., has been appointed manager of the Chicago Mechanical Rubber Branch.

Wittrup will serve under John H. Merrell, vice president of Raybestos-Manhattan, Inc., who is in charge of sales in the Mid-Western district.

IN line with their general expansion program, C. W. Velie, recently appointed sales representative for Manning, Maxwell & Moore, Inc., in the southwestern district at Tulsa, has been given an increased territory in the same district, but with headquarters transferred to Dallas. Velie's activities in his enlarged territory cover all of the products of the Ashcroft Gauge Division, Hancock Valve Division, Consolidated Safety Valve Division and



The Marley Company, Kansas City, Kansas, recently moved to its new warehouse and office building in the Fairfax industrial district and the new address is 3001 Fairfax Road. The new building is modern in every respect.

Check its Simplicity

STRAIGHT-LINE CONNECTION
Makes dis-assembling and inspection easy, without disturbing piping . . .

COCHRANE BUCKET TYPE STEAM TRAP

Design and construction assure efficient operation and long life. Quick, positive action discharges condensate through full orifice area, preventing wire drawing and erosion of valve and seat. Water seal provided by inverted discharge tube permits bucket to regain buoyancy before complete discharge. Valve snaps shut without blowing steam. Bucket and valve are the only moving parts. Write for Publication No. 2663 telling how to select proper trap sizes.

Cochrane Corporation, 3115 N. 17 St., Philadelphia, Pa.

COCHRANE
STRAIGHT-LINE BUCKET TRAP

Locate and Repair Diesel Engine Troubles Quickly and Easily.

Use the new wall chart prepared by Victor W. Pagé, M.S.A.E., the well known automotive engineer, SYSTEMATIC LOCATION OF DIESEL ENGINE TROUBLES.

Shows construction and all parts of typical engine and full system. Outlines all troubles causing lost power, misfiring, hard starting, noisy operation, smoking, etc. IDEAL FOR CLASSROOMS, WORKSHOPS AND GARAGES. A GUIDE TO LOGICAL TROUBLE SHOOTING.

Size 25" x 38". PRICE 50 cents.

Prepaid to Any Address—Special Price on Quantities

NORMAN W. HENLEY PUB. CO.
2 West 45th St., New York

PATENTED

Garlock announces the SPLIT-KLOZURE OIL SEAL

TO MEET the need for an Oil Seal that can be installed around the shaft rather than over the end of the shaft, GARLOCK has developed the new patented SPLIT-KLOZURE.

As shown in photograph above, the SPLIT-KLOZURE is split, or cut open. It is quickly applied by placing it around the shaft instead of dismantling the machine and sliding the seal over the end of the shaft, as is necessary with solid oil seals of the conventional type.

The SPLIT-KLOZURE is particularly suitable for heavy machinery and other installations in which down-time is expensive. For ordinary oil seal service we recommend the standard, solid GARLOCK KLOZURE. Write for catalogs.

THE GARLOCK PACKING CO.
Palmyra, New York
Tulsa, Oklahoma
Los Angeles, Calif.
Houston, Texas

GARLOCK

HIDDEN TREASURE FOR YOU HERE!

OIL and muck-covered valves, pipes, pipe-fittings and pumps may LOOK like Junk . . . BUT . . . it is just such useless-looking equipment that more and more producers and refiners are to-day salvaging the Oakite way . . . and literally saving thousands of dollars.

Perhaps *your* junk pile holds hidden treasure, too. Why not reclaim it by simple Oakite cleaning, and reconditioning? One oil company tells us Oakite materials have salvaged over $20,000 worth of equipment. Other companies report equally worth-while savings.

PROFIT BY OTHERS' EXPERIENCE

By using the recommended Oakite materials you can quickly SOAK equipment clean . . . without hand scraping or scrubbing. Much of this equipment can be put right back into service or placed in stock for re-use when needed. So successful are these low-cost Oakite methods of cleaning that you should know more about them. Won't you write us TODAY so we can place the data before you, all without obligation on your part?

Manufactured only by

OAKITE PRODUCTS, INC.

50B Thames St., New York, N. Y.

OAKITE *Certified cleaning*

MATERIALS & METHODS FOR EVERY CLEANING REQUIREMENT

American Schaeffer & Budenberg Instrument Division.

VAPOR RECOVERY SYSTEMS COMPANY of Compton, California, has underway an expansion program that includes the addition of 15,000 square feet of shop floor space and the tripling of present office space and facilities. The capital outlay for new buildings and machinery totals between $25,000 and $35,000. According to Frank V. Long, president, 168 complete Vapor Recovery Systems have been installed in the Long Beach area in recent months. Orders are being booked from Canada, Roumania and Poland, and with the approach of winter in the Southern hemisphere, complete systems are being installed in Peru, Bolivia, and other South American countries.

W. ROY WIDDOES has been appointed general manager of By-Products Steel Corporation, Coatesville, Pa. Born in Coatesville in January, 1895, Widdoes was educated at Coatesville High School and joined Lukens Steel Company in August 1912 as a clerk in the time department. In July, 1915, he became associated with the Reading Railroad but returned to the Lukens' organization later in the same year, serving in the purchasing department. In 1929 he was appointed assistant purchasing agent of Lukens Steel Company. In May, 1937, he joined By-Products Steel Corporation as assistant to R. W. Moffett, president, and served in that capacity until his recent appointment as general manager of the organization.

PERCY T. OLDHAM has been appointed manager of special sales for By-Products Steel Corporation, division of Lukens Steel Company, Coatesville, Pa.

Born in Wheeling, West Virginia, in September, 1890, Oldham received his education there and found his first employment as assistant county surveyor of Belmont County, Ohio. He was later field engineer for Wheeling Corrugating Company and Whittaker Glessner Company at the Wheeling, West Virginia, and Martins Ferry, Ohio, plants, both of which are now a part of Wheeling Steel Corporation.

In 1912 Oldham became supervising engineer with S. Diescher & Sons, consulting engineers, Pittsburgh, and in December, 1915, joined Lukens Steel Company as assistant construction engineer, serving in that capacity until 1925, when he was transferred to the sales department as manager of flanging sales. He occupied this position for several years, later becoming engaged in special sales work in which he remained until his recent appointment as manager of special sales for By-Products Steel Corporation.

He is a member of the American Society of Mechanical Engineers and of the Engineers Club of Philadelphia.

WITH its new rolling mill, representing an approximate investment of $4,000,000, rapidly nearing completion, Bridgeport Brass Company, one of the largest of America's independent brass mill products manufacturers, swings confidently into the 1938 scene.

The new mill covers a floor area of about 200,000 square feet and will be devoted to the production in sheet form of practically all the copper base alloys. It has special significance when viewed from two different standpoints. First, its construction has already given direct employ-

THE REAL COST OF A PACKING

is determined only by its

LENGTH OF LIFE IN SERVICE.

FOR THE OIL REFINERY

we offer

PELRO PACKING

For Gasoline, Naphtha and All Distillates of Petroleum.

Send for A B C CHART of Packing Services
Also
Free Working Sample.
State Size and Conditions of Service.

GREENE, TWEED & CO.
Sole Manufacturers
109 DUANE ST., New York

"Safety First-"
COMFORTABLE TOO!

Favorite Wood Sole Shoe of the OIL INDUSTRY

Orders Shipped Same Day Received

Consider the many possibilities of serious foot injuries facing your employees while at work . . . the costly and annoying service interruptions caused by these expensive foot injury delays . . . and the guaranteed foot protection features only offered by DAVENPORT Wood Sole Shoes. We believe your natural conclusion will be the same as countless other employers. And, that is—DAVENPORT WOOD SOLE SHOES ARE THE COMPLETE ANSWER TO BIG SAVINGS IN AVOIDING COSTLY FOOT INJURIES.

ONLY DAVENPORT WOOD SOLE SHOES have all these PROTECTION FEATURES

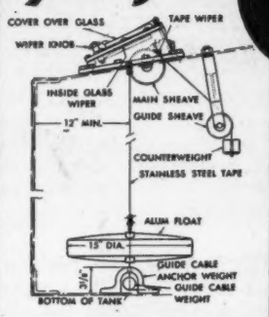
- **Uppers attached to soles with wire and staple stitching.**
- **Dust-proof gussets.**
- **Soft, pliable, sole leather counters.**
- **Seams double stitched with heavy wax thread.**
- **High quality, soft felt insoles.**

WRITE for our NEW LOW PRICES on quantity orders. Also FREE "Davenport Wood Sole Shoe Manual"—a reliable guide to foot protection for employees.

F. J. STAHMER SHOE COMPANY
2351 Boise Ave., Davenport, Iowa.
World's Largest Exclusive Mfrs. of Wood Sole Footwear

OCECO Gauges

...for LOW or HIGH PRESSURE TANKAGE...



• Oceco gauges eliminate slip-shod wasteful methods. They permit the taking of accurate tank readings, without relieving the pressure or exposing the gaugers to fumes—can be installed easily on existing or new tankage. Readings on Oceco Type 8 gauges are taken from the tank top ... on the Type 14 from the ground. Both types are of dependable Oceco design ... of non-corrosive construction ... and fitted with wipers to insure clear vision. Standard sizes are adapted for use on tanks with pressures ranging from less than an ounce to 75 pounds. Write for descriptive literature.

Specify
OCECO FITTINGS
your tanks
deserve the best

OCECO Fittings

THE JOHNSTON & JENNINGS CO.
OCECO DIVISION
885 Addison Road • Cleveland, Ohio
Engineering and Sales Services: NEW YORK • CHICAGO • PITTSBURGH
BEAUMONT, TEXAS • TULSA, OKLAHOMA • LOS ANGELES • OAKLAND, CALIF.

HAND BOOK

Butane-Propane Gases

Feature Contents of this Complete Reference Work

A Chronology of Liquid Gas Development; Physical Properties of the Liquefied Petroleum Gases; Properties of Butane-Propane Mixtures and Relation of Properties to Temperatures; Composition and Analytical Determination of Liquefied Petroleum Gases; The manufacture of Liquefied Petroleum Gas; Transportation of Liquefied Petroleum Gases; The Use of Butane and Propane with Manufactured Gas; Central Plants for Butane-Air Service; Central Plants for Undiluted Butane-Propane Vapor Service; Liquefied Petroleum Gases as Industrial fuels; Appliance Utilization of Liquefied Petroleum Gases; Bottled Gas Distribution of Liquefied Petroleum Gases; Table of flow of gas at low pressure through pipe lines; National Fire Protection Association's regulations; Catalogue Section; Buyer's Guide; Directory of Central Plants; Bibliography; Index.

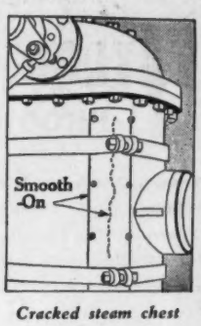
PRICE
$5.00
A Copy.

Send Check to

GULF PUBLISHING COMPANY
P. O. BOX 2811 HOUSTON, TEXAS

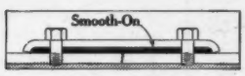
BADLY CRACKED PARTS

—Restored perfectly *with* SMOOTH-ON No. 1

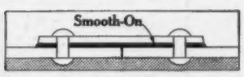


Cracked steam chest

MANY a cracked pressure cylinder, pump casing, steam chest, water jacket, heater shell, etc., that appeared to be a complete wreck has been restored to perfect usefulness with Smooth-On No. 1—and this at a cost of a few dollars in comparison with hundreds for disassembling, parts renewal and reassembling that could assure no better performance.

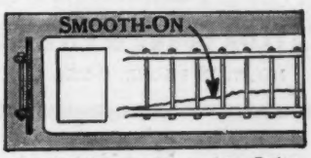


Soft Patch

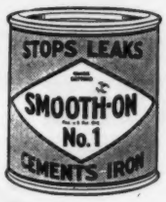


Hard Patch on boiler shell

Smooth-On achieves its saving through low repair material cost and shortening of operating interruptions. The engineer who is not familiar with the application of the Smooth-On Cements will find in the Smooth-On Handbook complete instructions for making these repairs. The instructions are copiously illustrated by diagrams which enable the user to pick the most practical application method and do a good job quickly and with maximum saving. Study the booklet, and then be further prepared for an emergency by getting a small supply of Smooth-On No. 1. Your first application will make you a Smooth-On enthusiast.



Cracked intercooler casting. Bolts used to pull edges of crack together



Get Smooth-On No. 1 in 1- or 5-lb. can or 25- or 100-lb. keg from your supply house or if necessary, direct from us.

Send for FREE booklet

SMOOTH-ON MFG. CO., Dept. 11, 570 Communipaw Ave., Jersey City, N. J.
Please send SMOOTH-ON HANDBOOK.
Name.....
Address.....
.....
.....

***Do it with* SMOOTH-ON**

CALL US

for the following

TAYLOR FORGE

PRODUCTS

Flanges, Weldells, Welding Reducers, Welding Tees, Flanged Unions, Special Flanges, Orifice Flange Unions, Boiler Nozzles, Welding Neck Nozzles, Spiral Welded and Spiral Riveted Pipe.

PRINCIPAL ITEMS STOCKED IN HOUSTON

THE CORBETT-WALLACE CORPORATION

2418 Winter Street
HOUSTON, TEXAS

Distributors for

TAYLOR FORGE & PIPE WORKS

HOUSTON PHONE: C-5327; L. D. 363

ment to an average of over 150 men per day since May 1, 1937, and provided a total of more than 28,300 man days' work during the past 10 months, and has involved the purchase of important quantities of building materials and the creation of labor in many fields at a time when such activity is needed. More than 1375 tons of structural steel, a total of more than 400,000 bricks, over 28,000 lights of glass with a sash area of 50,400 square feet, materials for 166,000 square feet of roof area and enormous quantities of other materials were utilized in the construction of the plant and adjoining office and laboratory building. An equally important and substantial outlay has been made for the purchase of modern machines, equipment and tools.

Second, it is important as an interesting departure from conventional brass rolling mill design. The direct flow of materials is the integral factor. In addition to allowing for the use of the most modern machinery and equipment available, it is planned with an eye to the growing importance of materials handling in efficient plant operation.

In this respect it is the most thoroughly systematized plant yet constructed in the industry and follows the straight line principle which has proved to be so effective in the steel industry. Smooth, continuous flow of metals throughout all stages, from ingots to finished rolls, automatic devices for handling to insure the utmost speed and economy, ready adaptability to varying production requirements—these are the outstanding features of the mill. Every unnecessary movement in the various steps—rolling, scalping, annealing, pickling, coiling, slitting, finishing and loading for shipment—has been eliminated to avoid waste of time and effort.

The added efficiency of the new rolling equipment not only allows the use of heavier castings but permits greater accuracy in the finished rolls. Oil-fired annealing furnaces add still further to the achievement of more accurate standards. This modern equipment is typical of every operating unit in the mill. The company's management expects that the mill will be in production by mid-summer.

M. N. DANNENBAUM COMPANY has been appointed sales representatives for Struthers-Wells Division of Struthers-Wells-Titusville Corporation in eastern Texas. Headquarters are at 202 Petroleum Building, Houston.

STRUTHERS-WELLS Division of Struthers-Wells-Titusville Corporation has announced appointment of P. H. Nicholls as representative in the southeastern states. His headquarters will be 1008 Norris Building, Atlanta, Georgia.

Valves and Fittings

THE WALWORTH COMPANY

The Walworth Company, 60 East 42nd St., New York, N. Y., has just published Walworth Catalog No. 89, a new 602-page catalog covering the wide line of Walworth valves, fittings, pipe and tools. Many added features are embodied in the catalog which should render it of increased usefulness to engineers, contractors, plant superintendents, purchasing agents and others interested in the Walworth line of products. In the center, for instance, is a red index permitting quick reference to each class of product listed in the book. Arrows on the red index pages point to the section markers at the beginning of each classified section. The new size makes possible a much less bulky format than before, so that the book is easier to handle. All of the principal items have an identifying code word for economy in cabling and telegraphing. The code words in the book are all in alphabetical order, so that messages can readily be deciphered.

Among the new sections not contained in previous catalogs are: the Marine Section; the Lubricated Plug Valve Section, with particular reference to fluids, gases and the like, with recommendations as to the types of lubricants best suited to them; the Walseal Section; the Hi-Test Cast Iron Pipe Section; the Fabricated Pipe Section, containing information of value in laying out piping jobs; the Piping Design and Engineering Data Section, including many original charts helpful in figuring the sizes and types of piping necessary for particular operating conditions; and the Soil Pipe Section.

In order to give the most comprehensive information possible on all Walworth products, the catalog specifies the type of metal used in the various parts of the valves and fittings. The Materials Section contains information concerning all types of metals used in Walworth products, complete data regarding working pressures as well as test pressures; and all the principal dimensions normally required either for laying out a job or allowing space necessary for operation of the valves. Copies of the catalog are available to those who request them on their company letterhead.

CORROSION plays no favorites. It never fails to find the weak link in the chain; the weak spot in the pipe line. When you weld with WeldELLS you eliminate *all* weak spots — those which would be attacked by corrosion as well as those which might yield to mechanical stresses due to expansion.

This expansion loop in an overhead vapor line is an example of this. The 20-inch WeldELLS are ¾" thick to allow for corrosion. Welded as only these engineered fittings can be welded, every part of this line is ready to do 100% battle against stress and corrosion.

With six features that are combined in no other welding fitting, WeldELLS are the final answer to a long existing need — the need for uniformly strong lines with joints that never leak — with joints as strong as the pipe — with smooth interiors that cut flow resistance — with smooth, sightly, easily insulated exteriors.

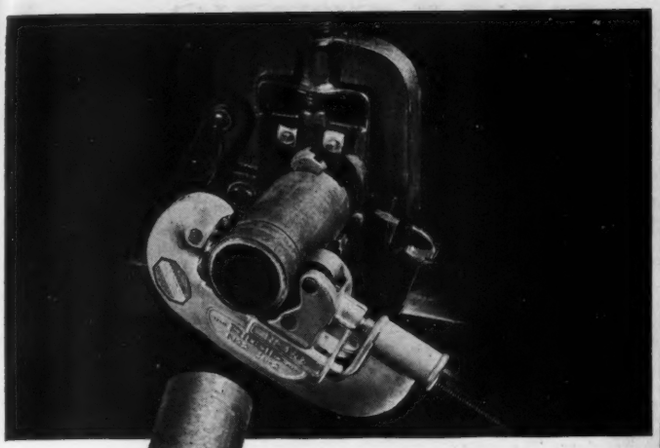
The line of WeldELLS and other Taylor Forge Fittings contains the largest range of sizes, types, and thicknesses. Large stocks are carried by distributors serving every branch of the oil industry.

TAYLOR FORGE & PIPE WORKS

General Offices and Works: P. O. Box 485, Chicago New York Office: 50 Church Street

TAYLOR FORGE *WeldELLS Seamless Pipe Fittings for Welding

*Trade Mark Registered



Quicker! Cleaner! Lower Cost Pipe Cutting

with this remarkable RIDGID Wheel-Blade Cutter...

Because every RIDGID tool is designed to save you bother and expense old-fashioned tools cause you, the millions of them now in use have saved billions of hours that used to be wasted.

That's true of this cutter. The thin bladed wheel — coined out of tool steel, hammered, heat-treated and assembled in a solid hub — has the extra stamina to keep on rolling readily cleanly through all kinds of pipe long after ordinary cutter wheels need replacing. And the housing is guaranteed warp-proof — always cuts true, twirls easily to your pipe size.

Try this tool of the smart buyer and the expert user. Save yourself time and expense with the RIDGID Cutter that gives you far more cuts per wheel-blade. Buy from your Supply House — now.

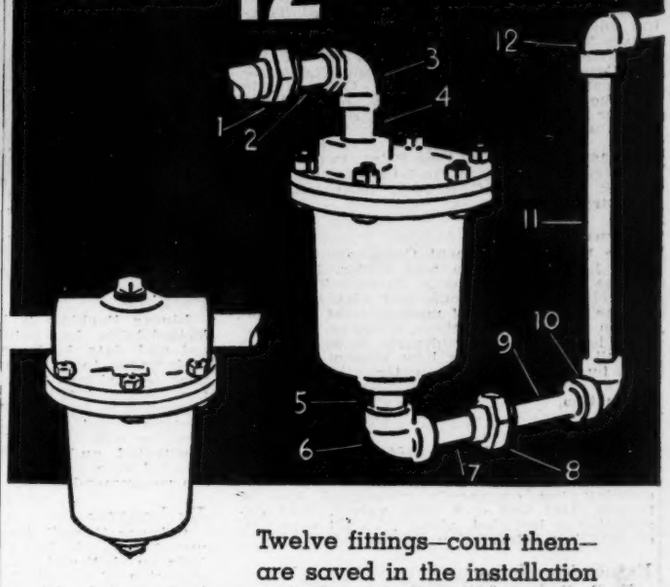
THE RIDGE TOOL CO., ELYRIA, O.

No More Wrench Housing Repairs

That guarantee saves you fully 75% of your pipe wrench repairs. Buy the RIDGID.

RIDGID PIPE TOOLS

"Short Cut" PIPING SAVES 12 FITTINGS



Twelve fittings—count them—are saved in the installation shown above by using an Anderson Super-Silvertop steam trap instead of an ordinary trap. This saving is due to the unique design of Super-Silvertop that permits straight-in-line piping or "short-cut" piping, instead of run-around piping.

In both cases above, the trap is an inverted bucket steam trap, but "short-cut" piping with Anderson Super-Silvertop gives a worthwhile saving in fittings.

Another feature of Anderson Super-Silvertop design is the longer lever arm which permits a larger valve orifice, hence an increased trap capacity. Then too, the smooth drilled passages insure positive handling of dirt and scale. That is why no strainer is necessary with Anderson Super-Silvertops.

Find out about the many other savings you can realize with Anderson Super-Silvertops—write for complete details.

THE V. D. ANDERSON CO.
1942 WEST 96th STREET • CLEVELAND, OHIO

You can send me that complete information on Super-Silvertops. If it shows me how to save money, I'm interested.

Name..... *Company*.....

Address..... *City and State*.....

CATALOGS . . . BULLETINS

Helpful Publications Which Manufacturers Will Be Glad to Send Free for the Asking

Electrical Equipment

General Electric Company, Schenectady, N. Y., has published the following new literature covering its electrical equipment items: GEA-2170A, Directional Distance Relays, Type GCX, Three Phase, Operating on Reactance; GEA-2003B, Use The Automatic Oil Circuit Recloser for Better Service in Emergencies; GEA-2823, High Accuracy Commercial Testing Instruments; GEA-1929A, 21 Low-Speed Drives That Have Been Modernized at a Saving with G-E Gear-Motors; GEA 2472, Pyranol Capacitators for Low-Voltage Industrial Applications; GEA-841H, A-C Magnetic Switches, Size One, Cr7006-d40, Full-Voltage Starter for Induction Motors; GEA-432C, Direct Current Generators and Exciters; GEA-1283A, G-E Cam-Operated Master Switches; GEA-2630, New G-E Dew-Point Potentiometer; GEA-2426A, Type Flo-1-Outdoor Oil-Blast Circuit Breakers; GES 1841, Instruments in Industry.

Instruments

The Brown Instrument Company, Philadelphia, has published a new folder, No. 94-1, on the Brown Pneumatic Remote Transmission with instant response and with safety for remote transmission of measurement and control in hazardous locations. Likewise the company is distributing Folder No. 80-36 "Jima is Right" which explains how Brown flow meters, by metering steam, water, oil, and other fluids, can bring many economies in power production.

Valves

Hancock Valve Division, Manning, Maxwell & Moore, Inc., Bridgeport, Conn., has published Bulletin 5-7000, illustrating and describing the company's redesigned line of forged steel and cast steel valves. Full description is included, along with all pertinent engineering information.

Expansion Joints

E. B. Badger & Sons Company, Boston, is distributing new literature describing the Badger Corrugated Type Expansion Joints designed for directed flexing and self-equalization. The Bulletin, No. 100 describes briefly and illustrates the various kinds of Badger Packless Expansion Joints, the history of this type of joint, the improvements brought out by Badger engineers, how to select the right type of joint for a given problem and includes list prices, dimensions and weights. The joints are made in copper and stainless steel.

Packings

Crane Packing Company, 1800 Cuyler Ave., Chicago, Ill., has released a new circular in colors on packings for reciprocating and centrifugal hot and light oil pumps with hard and medium hard steel plungers, valve stems, and the like. Large illustrations and concise descriptions, with engineering data conveniently arranged makes this circular a handy guide to those using such packings.

Tower

Haveg Corporation, Newark, Delaware, has published Bulletin C-1, describing in detail and giving constructional data on all types of reaction, absorption, fractionating towers made of Haveg. Complete information is also given on physical and chemical properties. This material is used to combat corrosion in such equipment as described.

Tools

Beaver Pipe Tools, Warren, Ohio, is distributing new literature announcing the Beaver Model B, a full range ⅛-inch to 2-inch pipe and bolt machine which may be purchased complete or in units. Also there is available a new condensed catalog of various types of pipe tools.

Equipment

Ingersol-Rand Company, 11 Broadway, New York, has published a new bulletin covering single, two, and three-stage Steam Jet Ejectors for removing air, gas or vapors from condensers and vacuum chambers. The 28-page bulletin explains the application and characteristics of ejectors and illustrates the operation and arrangement of all types of ejectors with either surface or barometric precoolers, inter and aftercoolers. The company has also published a new bulletin giving complete specifications and operating characteristics of the Cameron Class GT two-stage centrifugal pumps. Typical installations of these pumps are illustrated and described. This bulletin is Number 7067.

Packing

Linear Packing & Rubber Company, Inc., Philadelphia, has published a complete manual and data book on mechanical packings. References to this manual will enable any user of packings to select, quickly and easily the kind and type of packing best suited to his service and conditions. Sizes, weights, footage together with standard packaging practice are given. The packings are fully illustrated and described in detail, supplemented by a carefully compiled chart of service recommendations.

Exchangers

Griscom-Russell Company, 285 Madison Avenue, New York, has published a 16-page bulletin on shell-and-tube heat exchangers. Construction of a typical G-R Vaneflo exchanger is illustrated with references to the advantageous elements of its design and the exclusive features of the unit are fully described. Many different designs of stationary heads, floating heads, transverse baffles and longitudinal baffles are illustrated with statements of their application. Viscosity charts and other useful data are included.

Bolts

Victor Products Corporation, 2631 Belmont Avenue, Chicago, announces publication of its new complete catalog and price list. The 36-page volume contains complete information, illustrations, specifications and prices on the heat- and corrosion-resisting studs, bolts and nuts which are manufactured by the company in a wide range of metal and alloy specifications.

Safety Devices

Willson Products, Inc., Reading, Pa., has issued a new catalog of industrial safety devices. The illustrated catalog covers the complete line of eye, nose, throat and lung protectors, including more than 50 types of goggles for every conceivable purpose, a dozen welding handshields and helmets, seven Bureau of Mines approved types of dust respirators, air line respirators, abrasive helmets, etc.

Flanges

A. O. Smith Corporation, Milwaukee, Wisconsin, has distributed Bulletin 219, which is a highly technical article reprinted from "Heating, Piping and Air Conditioning" with the title "Strength and Design of Covers and Flanges for Pressure Vessels and Piping," written by T. McClean Jasper, H. Gregersen and A. M. Zoellmer of the research department of the corporation.

Packing

The Garlock Packing Company, Palmyra, New York, is distributing new literature covering a new development in his line of packings, called the Garlock Split-Klozure, which is a patented oil seal which is split or cut open and is applied by placing it around the shaft much as an ordinary packing ring is applied. It can be easily applied without dismantling the machine.

Speed Changer

Allis-Chalmers Manufacturing Company, Milwaukee, Wisconsin, is distributing Bulletin 1266, "New Horizons in Variable Speed Transmission," which describes and illustrates the company's newly developed speed changer applicable for equipment in industry where substantial change in speed is desirable to better control production.

Control

Leeds & Northrup Company, 4902 Stenton Avenue, Philadelphia, has published Catalog N-OOB, on Micromax Pneumatic Control. The new air-actuated control is presented in a 12-page bulletin, which concisely describes the control and the text is accompanied by large illustrations showing design, construction and application. The instrument has been proven in the field, especially on fractionating towers.

Refractory Cement

Quigley Company, Inc., 56 W. 45th Street, New York, is distributing Bulletin 322B, on Q-Chrome cement, made of selected Rhodesian Chromite containing a minimum of silica. The bulletin describes its resistance to chemically active slags which prevents penetration of slag, aiding in prolonging refractory life and reducing maintenance costs.

Boiler Meters

Bailey Meter Company, Cleveland, Ohio, is distributing Bulletin 46, a new 32-page brochure "Bailey Boiler Meters," which contains analyses of 7,000 combustion tests and describes the Bailey Boiler Meter in full detail, showing how it reduces boiler operating costs. Separate features included as furnace maintenance, smoke, ash pit losses or combustible in flue gases.

Sockets

Westinghouse Electric & Manufacturing Company, East Pittsburgh, Pa., has published Catalog section 43-600 on Westinghouse Type E Socket instruments for outdoor and indoor industrial plants. The 20-page, illustrated booklet describes the use of these instruments as an accurate and reliable means for determining what takes place in electrical systems. Application, economic advantages, construction details and the selection of sockets and accessories are explained. Tabulations and diagrams show styles and list prices.

Shims

Laminated Shim Company, Long Island City, New York, has published a new folder showing methods of securing quick, accurate adjustments of mechanical parts in the petroleum industry. The text covers refining and allied equipment maintenance problems.

Roofs

Johns-Manville, 22 East 42nd Street, New York, has revised its book "Johns-Manville Bonded Built-Up Roofs" to include information on the latest types of built-up roofing, and now contains, with its 36 pages, more than 40 complete detailed specifications on J-M Built-Up Roofs.

Burners

National Airoil Burner Company, Philadelphia, has published Bulletin 21, "Steam Atomizing Oil Burners," for use with heavy fuel oil or tar in boilers, stills, and other furnaces where compressed air is available for atomizing the oil. Photographs and line drawings supplement the text, which includes all pertinent engineering information.

Water Treating

The Elgin Softener Corporation, Elgin, Illinois, has published a new edition of a treatise on boiler water entitled "The Inside Story of Boiler Water Conditioning." The purpose of this practical bulletin is to explain in simple, non-technical terms the conditions most frequently encountered and to discuss the various methods of softening, treating and removing concentrations from the boiler.

USE THIS COUPON

.....
MANUFACTURER'S NAME

.....
MANUFACTURER'S ADDRESS

Please send me, without obligation, free booklet described in June, 1938, issue of REFINER AND NATURAL GASOLINE MANUFACTURER.

NAME.....

ADDRESS.....